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Metal Removal and Cyanide Destruction in Plating Wastewaters Using Particle Bed Electrodes

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The heart of the unit is an electrolytic cell with tin cathode and graphite anode particle bed electrodes and a cellophane separator. Sequential water flow through the electrodes gives concurrent removal of metal and cyanide under action of applied DC voltage. Design of the unit was based on design of and test results with a laboratory scale apparatus. Best removals were obtained with added NaCl as supporting electrolyte and anode bed effluent recirculation. Estimated total treatment costs, derived from a subsequent corporate-funded study, are $1.64/1000 ft^2 plated, with cadmium plating rinsewater use at 3.5 gpm for 2500 ft^2/hr and 40 hr/week operation.

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METAL REMOVAL AND CYANIDE DESTRUCTION IN PLATING WASTEWATERS USING PARTICLE BED ELECTRODES

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report concludes that electro-chemical techniques will be a vital element in the control of pollution from the metal finishing industry. The report describes the method, operational tests, and optimization data for the treatment of specific metal-cyanide wastewaters. For further information than what is described in this document please contact Fred Ellerbusch of the Industrial Pollution Control Division, IERL-Ci.

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ABSTRACT

A small (0.5 gpm) pilot-plant unit for metal and cyanide removal was constructed and demonstrated by operation on cadmium and zinc rinsewaters at a plating plant. With single-stage operation, 73% of an initial 22 ppm cadmium and 79% of an initial 44 ppm cyanide were removed. Retreatment of the effluent (equivalent to two-stage operation) gave overall removals of 95% of the cadmium and 94% of the cyanide. Similar two-stage treatment of zinc rinsewater gave overall removal of 75% of an initial 57 ppm zinc and 78% of an initial 195 ppm cyanide.

The heart of the unit is an electrolytic cell with tin cathode and graphite anode particle bed electrodes and a cellophane separator. Sequential water flow through the electrodes gives concurrent removal of metal and cyanide under action of applied D.C. voltage. Design of the unit was based on design of and test results with a laboratory scale apparatus. Best removals were obtained with added NaCl as supporting electrolyte and anode bed effluent recirculation. Estimated total treatment costs, derived from a subsequent corporate-funded study, are \$1.64/1000 ft^2 plated, with cadmium plating rinsewater use at 3.5 gpm for 2500 ft^2/hr and 40 hr/week operation.

CONTENTS

		Page
Forward		iii
Abstract		iv
I.	INTRODUCTION	1
II.	SUMMARY	2
III.	CONCLUSIONS	5
IV.	RECOMMENDATIONS	5
V.	THE ATOMICS INTERNATIONAL PBE PROCESS FOR REMOVING METALS AND CYANIDE FROM WASTEWATER	6
VI.	DESIGN OPTIMIZATION TESTS	9
	A. Introduction	9
	B. Analytical Methods	9
	C. Cell Design	9
	D. Optimization Test Results	11
	1. Water Conductivity	11
	2. Solution pH	11
	3. Flowrates	11
	4. N_2 Gas Agitation	11
	5. Recirculation	13
	6. Cathode Current Collector Spacing	13
	7. Anode Collector Material	13
	8. Separator	13

CONTENTS (Continued)

		Page
VII.	DESCRIPTION OF THE PILOT-PLANT UNIT	14
VIII.	RESULTS	20
	A. Operation of Pilot-Plant Unit with Synthetic Solutions	20
	1. Test Conditions	20
	2. Preliminary Testing for Design Verification (Tests with Multiple Anode Collector Rods)	22
	3. Results with Final Cell Design	22
	B. Operation of the Pilot-Plant Unit at the Plating Plant	32
	1. Cadmium Wastewater	32
	2. Tests with Zinc Wastewater	40
	3. Conclusions	46
IX.	APPLICATION OF THE PARTICLE BED ELECTRODE SYSTEM TO PLATING PLANT WASTEWATER TREATMENT	47
	A. Plating Wastewater Effluent Requirements	47
	B. Method of Application of AI's PBE System to Wastewater	47
	1. Multistage Operation	48
	2. Reuse of the Treated Wastewater	48
	3. Preliminary Cost Estimation	48
X.	REFERENCES	50

TABLES

		Page
1.	Summary of Plating Metal and Cyanide Removal	3
2.	AI Process Metal Removal Capability	8
3.	Selected Test Results - Laboratory Test Unit	12
4.	Results of Pilot-Plant Unit Test Runs at AI - Initial Test Runs with Seven Anode Collectors	23
5.	Results of Pilot-Plant Unit Test Runs at AI - Using One 2-1/4 in. Graphite Rod as Anode Collector and Sodium Sulfate as Supporting Electrolyte	24
6.	Results of Pilot-Plant Unit Test Runs at AI - Using 2-1/4 in. Graphite Rod as Anode Collector and Sodium Chloride as Supporting Electrolyte	26
7.	On-Site Heavy Metal and Cyanide Removal Demonstration Results - Preliminary Test Runs	34
8.	On-Site Heavy Metal and Cyanide Removal Demonstration Results - With New Separator and Na_2SO_4 as Supporting Electrolyte	36
9.	On-Site Heavy Metal and Cyanide Removal Demonstration Results - With New Separator and NaCl as Supporting Electrolyte	37
10.	On-Site Heavy Metal and Cyanide Removal Demonstration Results - Cadmium Line Wastewater Test Runs After Bed Regeneration	38
11.	Effect of the Supporting Electrolyte on Cadmium and Cyanide Regeneration	40
12.	On-Site Heavy Metal and Cyanide Removal Demonstration Results - Zinc Line Wastewater Test Runs After Bed Regeneration	45
13.	Preliminary Cost Estimation for the AI PBE System for In-Process Water Recycle Application	49

FIGURES

		Page
1.	Atomics International PBE Metal-Cyanide Removal Unit (Schematic)	7
2.	Laboratory Metal-Cyanide Removal Cell (Schematic)	10
3.	Schematic of Pilot-Plant Unit Cell	15
4.	Schematic Cross-Section of the Pilot-Plant Unit Cell Showing Electrode Collector Configurations	16
5.	Photo of Partly Assembled Pilot-Plant Unit	17
6.	Original Pilot-Plant Unit Configuration	18
7.	Pilot-Plant Unit On-Site at Plating Plant	19
8.	Heavy Metal and Cyanide Removal Pilot-Plant Unit Flow Diagram	21
9.	Effects of the Supporting Electrolytes on Cyanide Removal	28
10.	Effects of the Supporting Electrolytes on Cadmium Removal	29
11.	Effects of Flow Rates on Cadmium and Cyanide Removal	30
12.	Effects of Recirculation Through the Graphite Bed on Cadmium and Cyanide Removal	31
13.	Simplified Flow Diagram for In-Site Demonstration of the Atomics International PBE System	33
14.	Effects of Applied Current on Cyanide Removal - 2000 ppm NaCl Added	41
15.	Effects of Applied Current on Percent Cadmium Removal - 2000 ppm NaCl Added	42
16.	Effects of Initial Cyanide Concentration on Cyanide Removal - 2000 ppm Na_2SO_4 Added	43
17.	Effects of Initial Cyanide Concentration on Cyanide Removal - 2000 ppm NaCl Added	44

I. INTRODUCTION

The wastewaters from metal finishing operations contain various metals including Cr(VI), Ni, Cu, Cd, and Zn. These wastewaters originate in rinsing and related operations throughout the plating process. In these wastewaters, the metal may be in soluble form, usually complexed, e.g., with cyanide, or as solid hydroxides or oxides formed by hydrolysis in the diluted plating solution.

The Particle Bed Electrolysis (PBE) Metal-Cyanide Removal Process is designed to treat these wastewaters by removing the metals present in soluble form and destroying the cyanide ion. A small amount of salt is required in the removal process to impart electrolytic conductivity to the wastewater. No sludges are produced. The operating cost is relatively small. The metals may be recovered for re-use. Accordingly, this project was undertaken to demonstrate the process by designing and building a small metal-cyanide removal pilot plant unit, and operating it on-site at a plating plant.

II. SUMMARY

The Atomics International (AI) metal-cyanide removal process using particle-bed electrodes has been successfully demonstrated by operation of a pilot plant unit on cadmium and zinc rinsewaters at a plating plant. Using single-stage operation at a 0.5 gpm flowrate, with initial concentrations of 22 ppm Cd and 44 ppm CN^-, 73% cadmium and 79% cyanide removal were obtained. Retreatment of the effluent (equivalent to two-stage operation) yielded additional, comparable results, for overall removals of 95% of the cadmium and 94% of the cyanide. For the zinc plating-line rinsewaters, with initial concentrations of 57 ppm Zn and 195 ppm CN^-, single-stage treatment gave 49% Zn removal and 41% CN^- removal; with a second treatment, additional removal was effected for overall removals of 75% of the Zn and 78% of the CN^-.

The heart of this system is an electrolytic cell with a tin particle-bed cathode, a graphite particle-bed anode, and a cellophane separator in which relatively low voltage DC is used to remove soluble forms of metals and cyanide. With wastewater flow in sequence through the cathode bed and the anode bed, concurrent removal is obtained by deposition of the metal (or metals) in the cathode bed and destruction of the cyanide in the anode bed. No costly chemicals are required for the treatment, and no sludges are produced requiring disposal.

To accomplish the goals of this program, a metal-cyanide removal test unit was designed and fabricated, and after preliminary testing at Atomics International, was installed and operated at a plating plant. Simultaneously, laboratory studies and testing were carried out using a small two-chamber cell of design similar to the pilot plant unit cell. The objectives of this laboratory study were to improve the cell design and define the effect of process parameters (current, pH, water conductivity, flowrate, electrode collector spacing) on the removal process.

Laboratory tests showed that (within limits) removals of both metal (cadmium only tested) and cyanide were greater at higher current, pH, water conductivity, and (per unit of time) flowrate. Gas bubbling through the cell compartment also enhanced removal. Removals of 98% Cd and 84% CN^- were obtained under one set of test conditions with the (standard) initial concentrations of 35 ppm Cd and 125 ppm CN^-. Addition of a small amount of salt (e.g., 1000 ppm of Na_2SO_4) as supporting electrolyte was required for high removals. While better results were obtained at pH $\cong$ 11, good removals (66% Cd and 49% CN^-) were obtained at a pH of ~9.5.

The pilot plant unit cell resembled the laboratory cell, but was of 0.5 to 2.0 gpm nominal flow capacity. It was mounted on a transportable rack, along with required pumps, flowmeters, flow control devices, and filters,

for transport as a unit for on-site testing. During preliminary tests at Atomics International, using the same composition synthetic wastewater as used in the laboratory cell tests, it was found that better results were obtained using NaCl as supporting electrolyte than with Na_2SO_4. While a high (81%) Cd removal was obtained with Na_2SO_4 the best CN^- removal was only 34%. With NaCl, the best removals were obtained with recirculation through the graphite (anode) bed. In this case, 97% removal of the Cd and 77% removal of the CN^- at a 0.5 gpm flowrate were obtained.

In on-site tests, using filtered cadmium plating-line rinsewater, results similar to those on synthetic wastewater were obtained. After several modifications and repairs of transport damage, the unit was operated in numerous tests. Some of the results on both cadmium and zinc plating-line rinsewaters obtained with the final unit configuration are given in Table 1.

TABLE 1.

SUMMARY OF PLATING PLANT METAL AND CYANIDE REMOVAL RESULTS

Plating Line	Supporting Electrolyte (amount)	Initial Concentrations (ppm)		Percent Removals Effected					
		Metal	Cyanide	1st Pass		2nd Pass		Overall	
		M	CN	M	CN	M	CN	M	CN
Cd	NaCl (2000 ppm)	22	44	73	79	91	69	95	94
	Na_2SO_4 (2000 ppm)	56	90	27	44	47	41	58	67
Zn	NaCl (2000 ppm)	57	195	49	41	58	63	75	78
	Na_2SO_4 (2000 ppm)	63	120	70	33	46	36	81	55

The process may be used for treatment and disposal of wastewaters, or it may be used at lower cost in processing rinsewater for reuse, where the rinsewater concentrations of metal and cyanide are maintained at or below specified levels. With a three-stage system to treat the rinsewater for recycle with the cyanide level down to 13 ppm from an initial 110 ppm, about 7 kwh/1000 gal would be required. With electricity at 4¢/kwh, and savings in water (at 25¢/1000 gal) total costs (capital and operating) of 1000 gal of wastewater are estimated for a 5 gpm recycle system at $2.11/1000 gal.

These cost estimates were based on pilot-plant unit design. A more accurate cost estimation obtained subsequent to the conclusion of the project

is reported. Under corporate funding, AI derived a detailed design for a commercial-type unit and corresponding costs. With rinsewater use at 3.5 gpm for 2500 ft^2/hr cadmium plating, with 40 hr a week operation, total costs of \$1.64/1000 ft^2 plated were derived.

In summary, the Atomics International PBE metal-cyanide removal system has been successfully demonstrated in on-site operation, and appears to offer a technically and economically feasible method for treating metal finishing wastewaters.

III. CONCLUSIONS

The Atomics International particle bed electrode (PBE) system has been shown by on-site demonstration at a plating plant to be an effective method for removing both heavy metals and cyanide from wastewater. A preliminary economic assessment indicated that the process could be utilized at reasonable costs. This was confirmed in a subsequent, considerably more detailed corporate-funded design and economic evaluation.

IV. RECOMMENDATIONS

It is recommended that a large test unit based on the commercial-type design for a complete system and with complete instrumentation and controls be designed, built, and tested on several suitable plating lines. These tests will involve continuous operation with minimal operator attention. At the same time, optimization studies on a laboratory unit should be carried out for cathode bed regeneration and metal recovery.

V. THE ATOMICS INTERNATIONAL PBE PROCESS FOR REMOVING METALS AND CYANIDE FROM WASTEWATER

The Atomics International PBE Metal-Cyanide Removal Process employs an electrolytic cell to treat waters containing soluble forms of heavy metals and cyanide. Figure 1 shows the basic components of such a removal unit in schematic fashion. The cell consists of a particle bed anode and cathode whose bed and current collector materials are fairly good electronic conductors. A separator (electronic nonconductor) which permits passage of ions while preventing bulk flow of water is interposed between the anode and cathode beds.

In operation, a DC potential is applied to the cell current collectors, as shown in Figure 1. The water to be treated is passed through the cell, so that it flows first through one bed and then the other. In the illustration, the flow is first through the cathode compartment (bed), then through the anode compartment (bed). In the cathode bed, electrochemical reduction occurs, resulting in metal deposition from solution. In the anode, oxidation occurs, resulting in the destruction of cyanide ion. Thus, the net result is concurrent metal and cyanide removal.

The reactions occuring at the cathode are:

$$M^{+n} + ne^- \longrightarrow M^0$$

for uncomplexed soluble metallic ions, or,

$$M(CN)_x^{(x-n)-} + ne^- \longrightarrow M^0 + xCN^-$$

for metallic ions in cyanide complex form. Also at the cathode, hydrogen evolution occurs to an extent depending on (1) rate of transport of metallic species to the cathode surface, (2) pH, (3) current, (4) applied potential, and (5) nature of the surface, according to the equation:

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

A certain minimal electrolytic conductivity is required of the wastewater to be treated depending primarily on cell geometry. Additions of small amounts of salt (e.g., 500 to 2000 ppm of Na_2SO_4 or NaCl) may be made to the incoming stream to obtain the required conductivity.

Tin had been found during previous studies at Atomics International to be a superior material for the cathode bed.[1] Its combination of corrosion

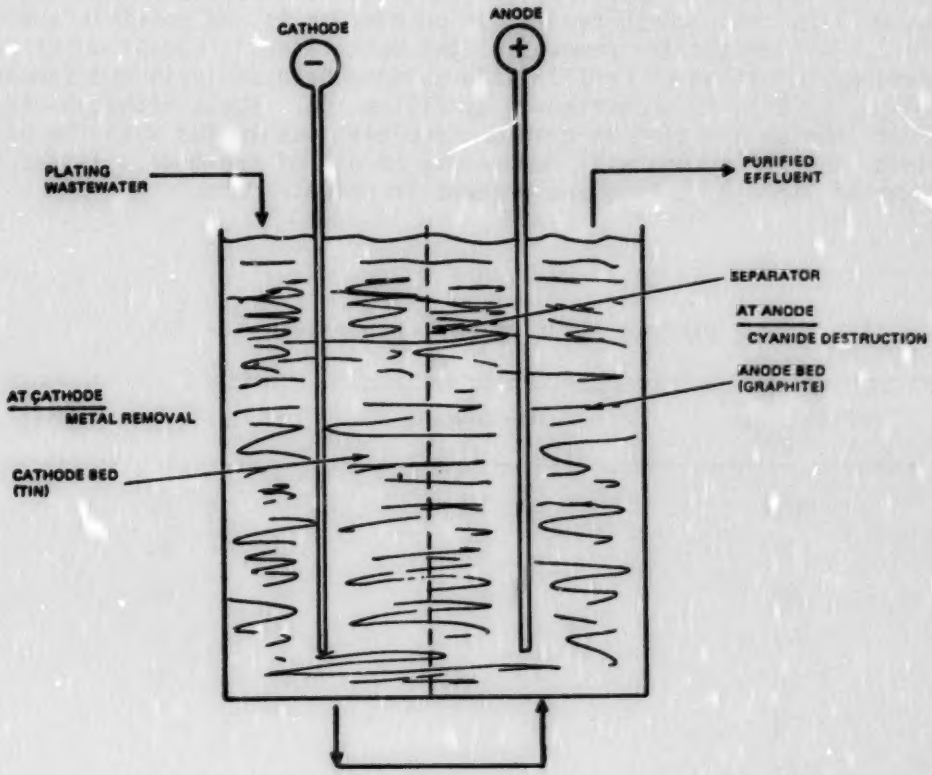

Figure 1. Atomics International PBE Metal-Cyanide Removal Unit (Schematic)

resistance and high hydrogen overvoltage is desirable. For the anode bed, graphite appears to be superior to most materials. It resists oxidation, even by Cl_2, and has a high overvoltage for oxygen evolution. Stainless steel was suitable and was used as a cathode collector; graphite was used as the anode collector.

A variant of the present process for removal of heavy metals only was developed earlier at AI[1] and studied for the State of California.[2] In the metal removal process, the nature of the anodic process is different so that different cell designs may be required. The metals which can be removed as well as those whose removal is unknown or is not possible are shown in Table 2. All metals are removed as the metal itself, except Cr(VI) which is removed by formation of Cr(III) with subsequent hydrolysis and formation of $Cr(OH)_3$. $Cr(OH)_3$ is then removed by filtration. Thus, although only the removal of cadmium and zinc as cyanide complexes was tested with the pilot-plant unit, the PBE system will remove any or all of the metals listed in the column of Table 2 if they are present in soluble form.

TABLE 2

AI PROCESS METAL REMOVAL CAPABILITY [1,2]

Will Remove	May Remove	Will not Remove
Hg	Sn	As
Pb	Sb	Ti
Au	Bi	Mn
Ag	Ta	
Cd	Co	
Cu		
Zn		
Fe		
Cr		
Ni (in Cl^-)		

VI. DESIGN OPTIMIZATION TESTS

A. INTRODUCTION

A series of laboratory tests was carried out to explore the effect of cell design features and of several key operating factors in determining the rate of metal and cyanide removal, so that the results could be used in the design of the on-site pilot-plant unit. After several discussions with representatives of the local metal finishers and visits to several sites, a plating plant was selected for the demonstration site. Samples were taken and analyses were made of several of their wastewaters. A decision was then made to initiate the design optimization testing program using a synthetic wastewater based on cadmium line drag-out rinsewater which contained about 35 ppm cadmium and 125 ppm cyanide. Testing with this synthetic wastewater would provide results representative of the system for removal of cyanide and cadmium ions from the actual wastewater.

B. ANALYTICAL METHODS

A procedure was worked out for use of a cyanide specific electrode in conjunction with an ion meter for rapid analyses of cyanide ion in the treated solutions. Cadmium interference was not evident if pH was adjusted to 13 for measurement. Atomic absorption spectrometry, AAS, was used for the analyses of Cd^{+2} ions and Zn^{+2} ions.

C. CELL DESIGN

In cyanide removal tests in a laboratory cell, a Union Carbide UCAR Grade BB-7, 3x20 mesh granular graphite gave results comparable to those with a UCAR BB-6 8x20 mesh granular graphite and was judged to be physically more suitable than the finer material. The BB-7 material was accordingly selected for further laboratory tests and for use in the pilot plant unit.

A small cell was designed and constructed for testing concurrent Cd^{+2} and CN^- removal. It consisted of a 22 in. long cylindrical Plexiglas outer shell with suitable fittings, covers, etc. This is shown schematically in Figure 2. A central, cylindrical anode compartment is separated from the outer cathode compartment by a separator. The separator is a 1.5 mil thick Cellophane sheet protected by an inner stainless steel screen and an outer plastic screen. Tin shot (8x20 mesh) was used in the cathode bed with eleven 1/8 in. stainless steel rod collectors and the Union Carbide 3x20 mesh granular graphite was used in the anode bed with a single 3/8 in. graphite rod collector.

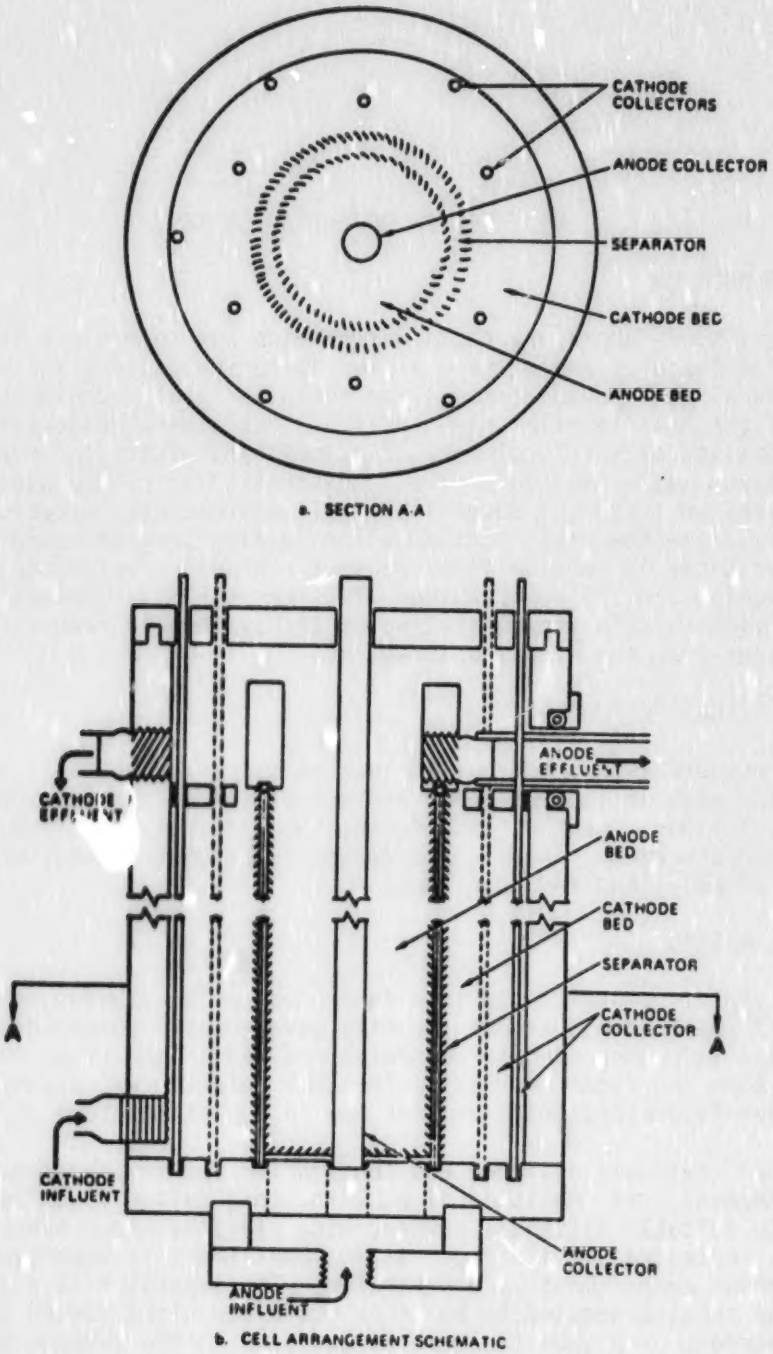

Figure 2. Laboratory Metal-Cyanide Removal Cell (Schematic)

D. OPTIMIZATION TEST RESULTS

A series of laboratory tests was performed to evaluate the effect of several critical design and operating parameters on the concurrent removal of cadmium and cyanide from a synthetic plating wastewater. The important parameters investigated included 1) water conductivity (1.0 to 3.0 millimhos/cm), 2) pH (9.5 and 11.0), 3) flowrate (140 to 1000 ml/min), 4) N_2 gas agitation, 5) recirculation, 6) cathode (tin bed) current collector spacing (11, 6, or 3 collectors), 7) anode (graphite-bed) collector material (graphite and stainless steel). A selected group of data from these laboratory tests indicates the effects of various parameters on Cd^{+2} and CN^- removal. These are given in Table 3. The pertinent observations were as follows:

1. Water Conductivity

Water conductivity was found to play a significant role in removal effectiveness: this may be seen by comparing the results of Run No. 20 with those of Run No. 8. It was also found that removal of both Cd^{+2} and CN^- increased with increased current to a limiting value. This value, and the corresponding percent removal, were higher with the more conductive water. In addition, the applied voltage to maintain a given current was lower with the more conductive water. The addition of a small amount of salts (e.g., NaCl or Na_2SO_4) to the plating wastewater before treatment would enhance the removal results of a given cell design.

2. Solution pH

The effect of wastewater pH may be seen by comparing results from Run No. 2 and Run No. 20 (Table 3). At otherwise similar conditions, a (14%) higher Cd^{+2} and a (43%) higher CN^- removal were obtained at pH = 11 than at pH = 9.5. Nonetheless, the removal effected at the lower pH was substantial.

3. Flowrates

Tests in the laboratory unit (see the results of Run Nos. 20 and 24, Table 3), in which flowrates were increased up to sevenfold, showed both cadmium and cyanide removal rates (amount removed per unit residence time) were increased by factors of up to 3.5 and 2.5, respectively. As noted above, removal has been found to have a limit with current, no further removal being effected with further increase in current. The value of this limiting current was found to increase with increasing flowrate.

4. N_2 Gas Agitation

As may be seen from the results of Run No. 25, gas bubbling with nitrogen, at a given flowrate and current, was found to decrease the required cell voltage somewhat and to increase the extent of removal significantly (by 2X for Cd^{+2} and 25% for CN^-); these are both desirable effects. While this approach may not be economically feasible using nitrogen, use of air bubbling in the anode (cyanide removal) compartment may be feasible.

TABLE 3

SELECTED TEST RESULTS - LABORATORY TEST UNIT

Run	pH	Na_2SO_4 Added (mg/ℓ)	Flow Rate (ml/min)	Current (amp)	Voltage (v)	Percent Removal Cd	Percent Removal CN	Comments
2	10.9	1000	140	0.5	1.99	69	4	Shows effect of increased current
				2	4.45	75	70	
				4	5.52	91	83	
				6	6.13	98	84	
20	9.7	1000	140	2	4.90	66	49	Shows effect of lower pH
8	9.5	200	140	2	4.97	49	30	Shows effect of lower conductivity
20	9.7	1000	140	2	4.41	66	49	Shows effect of flowrate
	9.7	1000	660	2	4.37	42	27	
24	9.8	1000	1000	2	3.97	33	10	
25	9.8	1000	220	2	4.93	33	36	*N_2 gas bubbled through chambers
			220*	2	4.14	64	45	
			1000	6	7.03	23	16	
			1000*	6	6.41	54	20	

*Initial concentrations: 125 ppm CN and 35 ppm Cd

5. Recirculation

In principle, recirculation of a fraction of the water (i.e., the return of part of the cathode effluent to the cathode influent and/or part of the anode effluent to the anode influent) should improve removal* by increasing transport of the species to be removed to the electrode bed surface. With recirculation in both cathode and anode compartments, no evident improvement was noted under test conditions (pH = 9.7, conductivity = 2.5 millimhos/cm, current = 2 amp and 6 amp) over recirculation ratios of 1:1, 2:1, and 4:1. It should be noted that the initial concentration of the species being removed decreases with increased recirculation ratio. As the rate of removal is a function of the concentration, these effects may have cancelled out in this particular case. Further testing of recirculation in the pilot plant unit was still warranted.

6. Cathode Current Collector Spacing

Reducing the number of cathode collectors from 11 to 6 resulted in a higher voltage (7.1 v cf 6.1 v at 6 amp) under otherwise identical conditions. This pointed out the need for adequate contacting of the current collectors with the beds.

7. Anode Collector Material

Quite satisfactory cyanide removal results have been obtained using a graphite anode collector. Improved cyanide removal was obtained by use of a stainless steel anode collector. In a set of tests, 75% CN^- removal was observed compared with 38% removal under similar conditions with a graphite anode collector. To optimize the process, therefore, tests were run to see if stainless steel would hold up under extended testing. A 1000 ppm NaCl solution adjusted to pH = 9.5 was used at a 140 ml/min flowrate at a cell current of 4 amp for 15 hr. The 304 SS rod was corroded generally and showed some pitting attack. As part of an effort to find an improved anode collector, a series of small scale short time screening tests were made with metal rods as anodes in a beaker. A test solution of 1000 ppm NaCl + 1000 ppm Na_2SO_4 was used. Of the three dozen metals** and alloys examined, all, without exception, either dissolved or developed a very high resistance when made anodic. Based on these results, graphite remains the most satisfactory anode collector available and was used in the demonstration unit.

8. Separator

The separator of the laboratory test cell was found to have suffered accumulation of ion oxides evidently from the stainless steel screen serving to support the separator. It was found that this corrosion problem can be avoided by replacing the stainless steel screen with a plastic screen.

*No resolubilization of metal should occur while the required D.C. potential is applied to the cell.

**These included Ti, Ta, Nb, various stainless steels, Hastelloys, Inconels, Incoloys, and others.

VII. DESCRIPTION OF THE PILOT-PLANT UNIT

The design of the pilot-plant unit metal-cyanide removal cell is shown in overall schematic fashion in Figure 3. This cell is similar in configuration to the laboratory test unit (see Figure 2). The cell is of cylindrical shape, with an outer cathode compartment filled with tin shot, an inner anode compartment filled with granular graphite and a cellophane separator protected with a plastic screen, and supported on an epoxy coated stainless steel screen. This epoxy coated stainless steel screen was later replaced with a plastic screen to prevent corrosion problems. In the pilot-plant unit cell the 12 stainless steel rod cathode current collectors are evenly spaced at the periphery of the compartment; seven graphite anode current collectors were positioned with one central rod and an outer hexagonal array. These seven anode collectors were later replaced with a single central collector of 2-1/4" diameter for better structure support and cell operation. Figure 4 shows the electrode collector configurations in the initial and final cell designs. A photograph of the partly assembled cell is shown in Figure 5. The stainless steel rod cathode current collectors are shown as a cage-like structure to the right of the Plexiglas cased cell. The horizontal rings (of rubber) on the cathode collector assembly and on the screened separator (in the cell) are designed to baffle flow through the cathode compartment, insuring that all the water is properly treated. Instead of one-piece rod or rods, the graphite anode collector or collectors were assembled from 1 ft sections of graphite rods. The cell, in a 9 in. diam Plexiglas shell, has anode and cathode chambers about 6 ft long. The removal unit cell design permits either upflow or downflow in the cathodic (metal removal) and anodic (cyanide removal) compartments. For ease of operation, only upflow was used in these tests.

During initial operation at Atomics International, a number of changes were made to improve the performance and reliability of the unit. Several leaks were found between the electrode compartments; these were corrected by calking the ends of the membrane separator. In anticipation of a potential problem, a porous, cushioned outer covering was installed over the separator assembly to prevent penetration of the cellophane separator membrane by sharp-edged protrusions on the cathode tin particles.

The original plan was for all auxiliary equipment to be mounted on the base or back board of the frame. These pieces of auxiliary equipment include the DC power supply, pump, flowmeter, regenerant solution storage tank, and requisite valves and tubing. The original overall pilot plant unit configuration planned is shown in Figure 6. With the installation of liquid level control tank, a second pump, and associated gear, changes were made in the position of several components. Also, the power supply was mounted external to the frame. The unit in final form and operating on-site at the plating plant is shown in Figure 7.

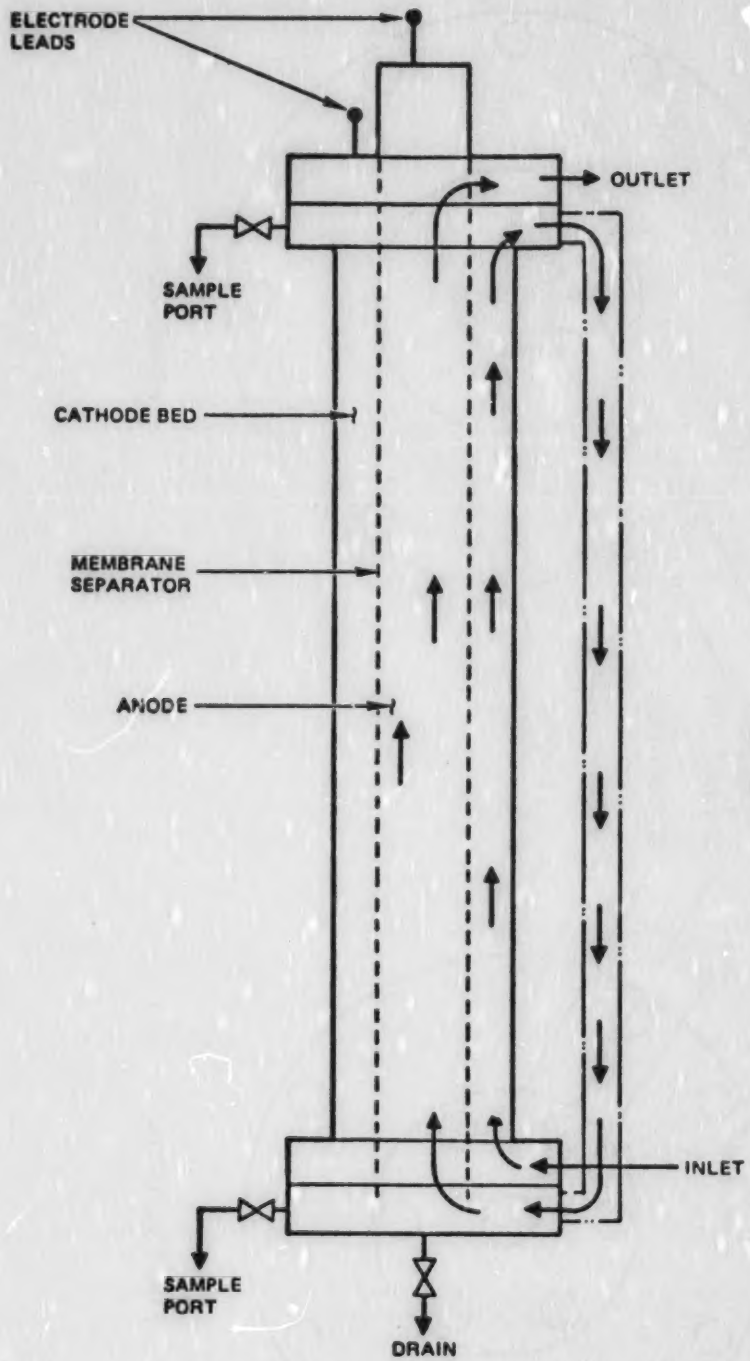

Figure 3. Schematic of Pilot-Plant Unit Cell

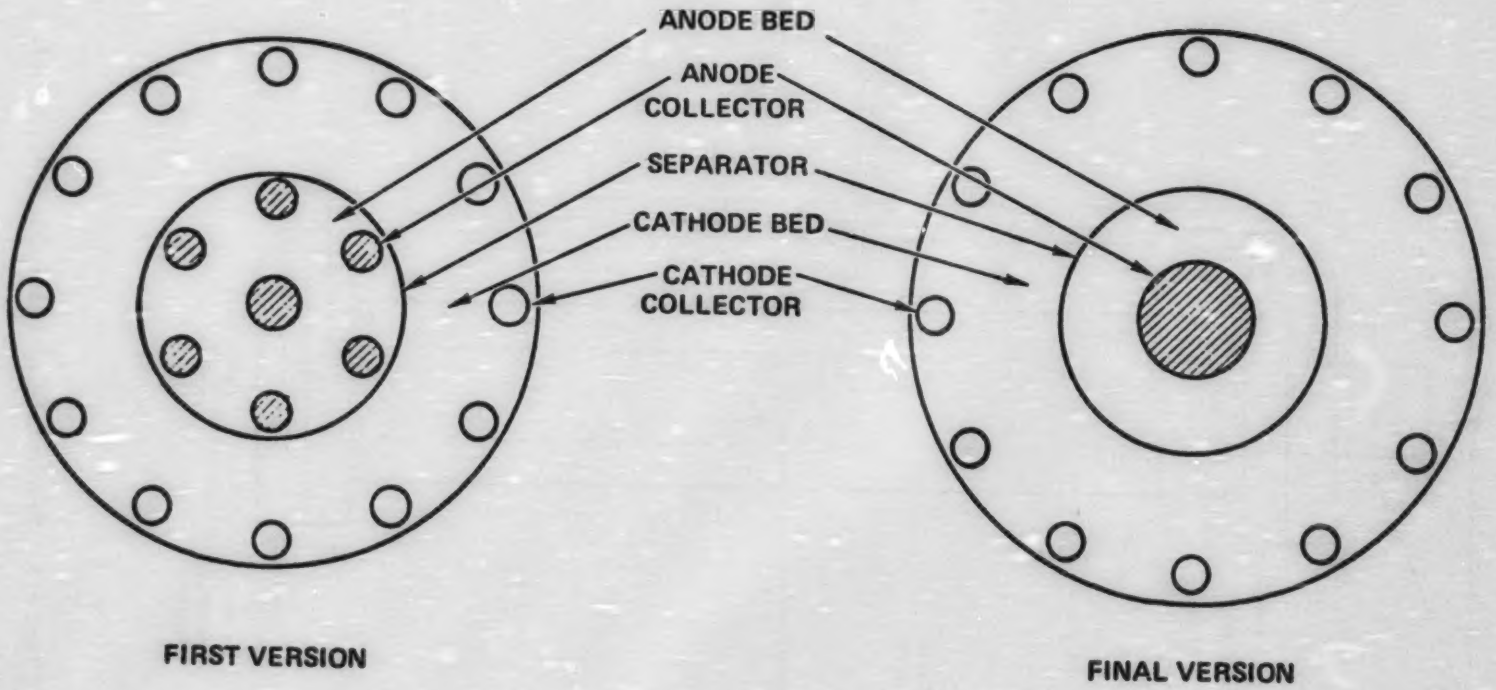

Figure 4. Schematic Cross-Section of the Pilot-Plant Unit Cell Showing Electrode Collector Configurations

Figure 5. Photo of Partly Assembled Pilot-Plant Unit

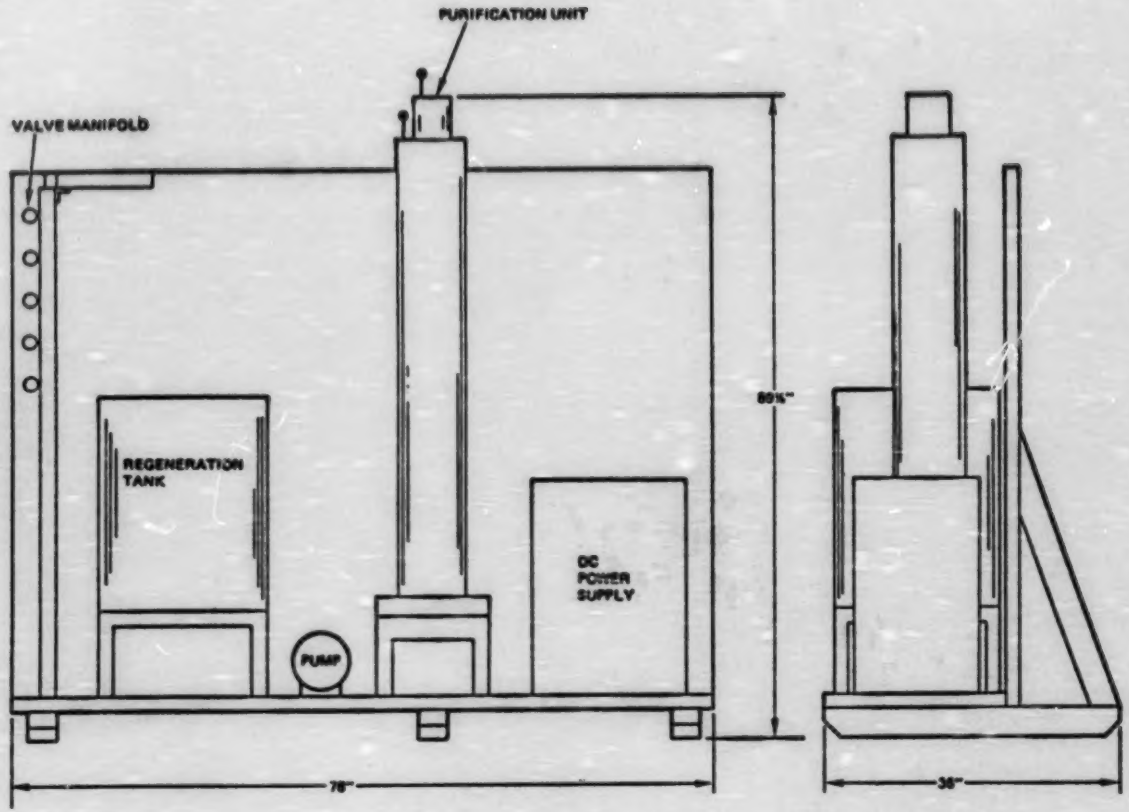

Figure 6. Original Pilot-Plant Unit Configuration

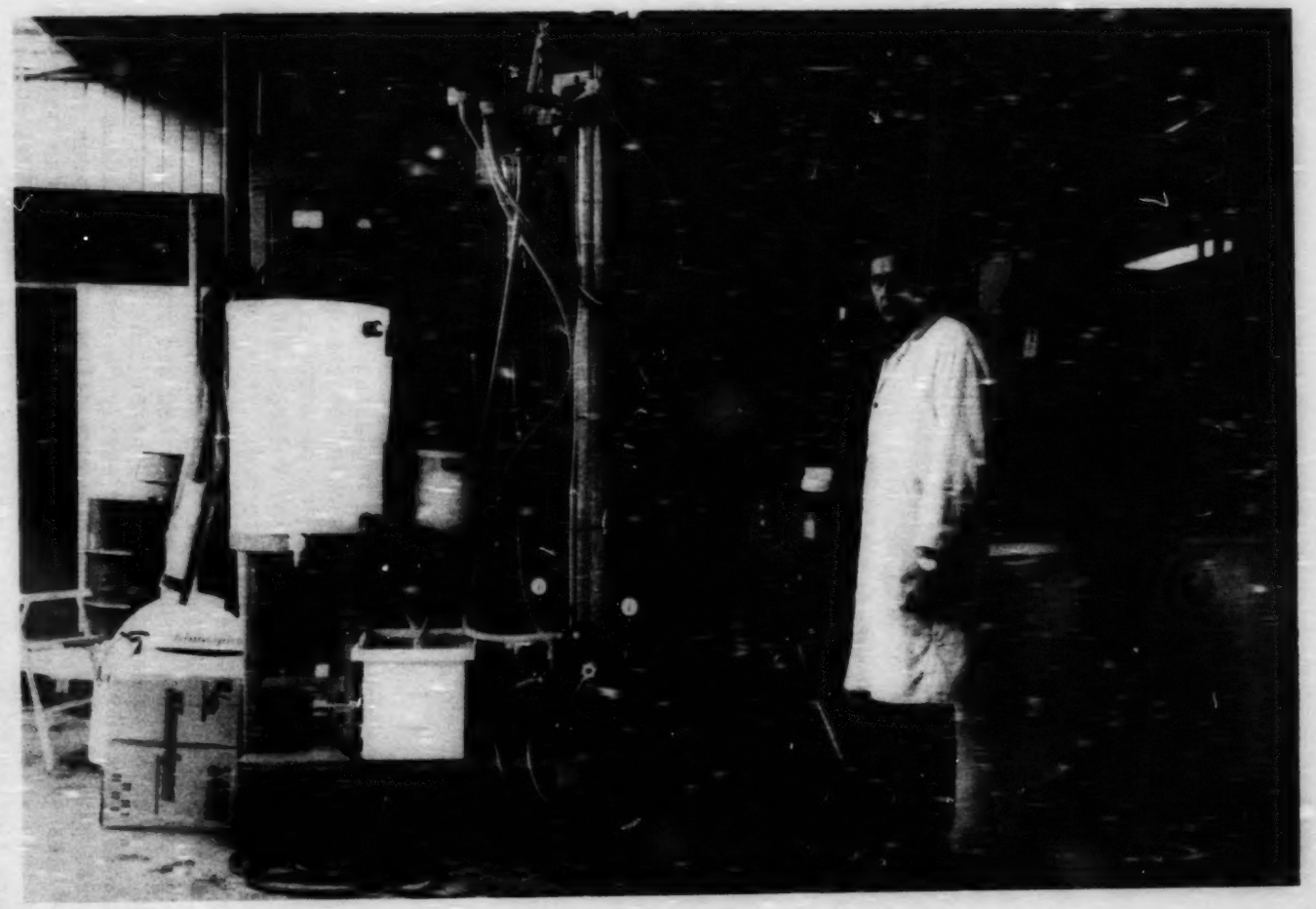

Figure 7. Pilot-Plant Unit On-Site at Plating Plant

VIII. RESULTS

A. OPERATION OF PILOT-PLANT UNIT WITH SYNTHETIC SOLUTIONS

1. Test Conditions

Prior to the on-site demonstration, the Pilot-Plant Unit was tested at Atomics International using a synthetic wastewater prepared by dissolving 59.4 grams of KCN and 15.4 grams of $3CdSO_4 \cdot 8H_2O$ in 50 gallons of distilled water. The resulting synthetic wastewater consisted of about 35 ppm of Cd^{++} and 125 ppm of CN^-. Na_2SO_4 or NaCl was also added as the supporting electrolyte. The pH of this synthetic wastewater was about 10.5. The conductivity of the synthetic wastewater varied from 2.3 to 4.9 millimhos per centimeter, depending on the amount and type of the supporting electrolyte used.

During the test runs, the synthetic wastewater from a 50-gal supply drum was pumped at a fixed flowrate--e.g., 0.5 gpm, 1.0 gpm, or 1.5 gpm--into the tin bed of the test cell. The effluent from the tin bed was collected in a liquid-level control tank, and then pumped into the graphite bed of the test cell. A bypass valve, whose opening was adjusted by a floating arm in the liquid-level control tank, maintained the liquid level in the control tank. The effluent from the graphite bed went to a treated wastewater collection drum. A portion of the effluent from the graphite bed could be diverted to the liquid-level control tank for recirculation through the graphite bed. During the test run, current was kept constant for at least 15 minutes prior to sample collection to ensure that steady-state conditions had been attained.

Feed samples were taken both at the beginning and just before the end of each test run. Treated wastewater samples of the graphite bed effluent were taken just before change in operating parameters. The operating parameters were current and its corresponding voltage, flowrate, and recirculation ratio (if any) through the graphite bed. Prior to the actual test runs, a dye test was made to determine if there were any significant cross-flow through the separator of the test cell. This was carried out by recirculating methylene blue solution through the tin bed and tap water through the graphite bed. No color appeared in the tap water tank. A hydraulic test showed that equal flow in both beds could easily be obtained. Flows varied from 0.2 to 2.0 gpm. At 2.0 gpm, the pressure differential between the tin and graphite beds exceeded 5 psi with the pressure drop in the tin bed being greater. As this value may put undue stress on the cell separator, actual test runs were limited to a maximum flowrate of 1.5 gpm. Details of the hydraulic system are shown in Figure 8.

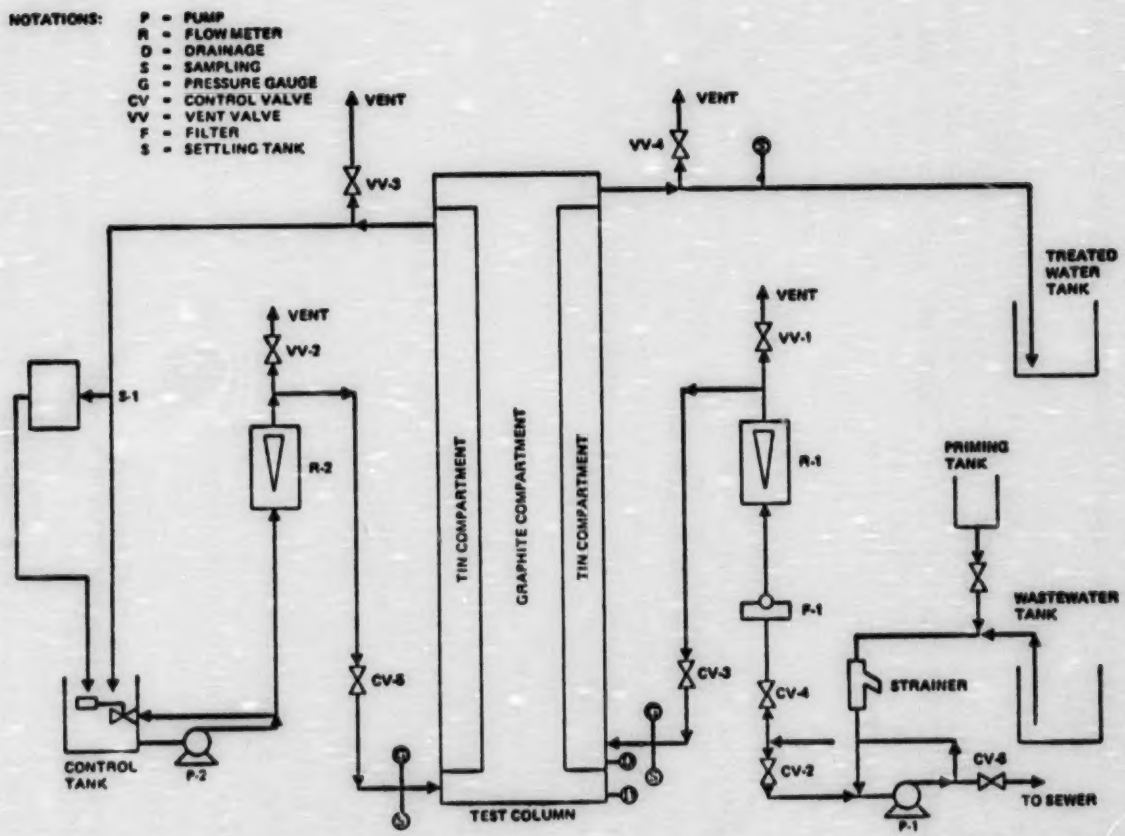

Figure 8. Heavy Metal and Cyanide Removal Pilot-Plant Unit Flow Diagram

2. Preliminary Testing for Design Verification (Tests with Multiple Anode Collector Rods)

In the first series of tests, as described above, the cell configuration with seven graphite anode current collector rods was used. The top view of this test cell is shown in Figure 4. The results varied from 6 to 89% for cadmium removal and 11 to 25% for cyanide removal. Details of the test results are shown in Table 4.

It was observed in most cases that cadmium removal increased somewhat with increased current, while cyanide removal decreased with higher currents. It was concluded that relatively simple cell modifications should improve cyanide and cadmium removals. Before any change was made, several tests were run to check the effects of graphite anode collector rod spacing on the cadmium and cyanide removals. These tests were carried out by rearranging the contacts on the graphite rods. Three different rod configurations were tested. These were: (1) a central rod alone, (2) one central rod and an outer triangle array, and (3) six rods in an outer hexagonal array alone. The results obtained using various graphite rod configurations were not conclusive. However, a simple theoretical evaluation of current and potential patterns in the cell suggested that a single central rod of adequate current handling capacity was the most effective configuration. For this reason and for better structural support, the test cell was modified by replacing the seven anode rods with a single, central rod of 2-1/4" diameter. This modified test cell resembled a scaled-up version of the small lab unit described in Section VI-C.

3. Results with Final Cell Design

a. Cell Design Changes

As noted above, the pilot-plant test cell was modified by replacing the seven graphite rods with a single centrally located 2-1/4 in. diameter graphite anode collector rod. Four 14 in. single segments were threaded together to form this rod; a 1/2 in. diameter stainless steel rod at the top was threaded into the graphite for electrical contact, while a short 1/2 in. diameter graphite rod was threaded into the large graphite rod at the bottom for positioning it in a slot in the plastic base. The top view of this cell with the modified collector rod arrangement is shown in Figure 4.

b. Test Conditions

Tests of cadmium and cyanide removals were again carried out using the synthetic wastewater described above. The test results obtained using Na_2SO_4 as the supporting electrolyte are given in Table 5. Results were considerably better with 2000 ppm of Na_2SO_4 than with 1000 ppm. While cadmium removal increased, or, in some cases, remained nearly constant with increased current, in all cases, cyanide removal decreased with increased current.

To increase cyanide removal, test runs were made using NaCl as the supporting electrolyte. It was believed that with $SO_4^{=}$, the CN^- oxidation was occurring only by direct electrode reaction at the graphite surface. Evolution

TABLE 4

RESULTS OF PILOT-PLANT UNIT TEST RUNS AT AI - INITIAL TEST RUNS WITH SEVEN ANODE COLLECTORS

Run No.	Solution Conditions			Flow Rate (gpm)	Current (amp)	Voltage (volts)	% Cd^{++} Removal	% CN^- Removal	Remarks
	CN^- (ppm)	Cd^{++} (ppm)	pH/ 10^{-} ctivity cm^{-1}						
D-2	125	35	10.9/2.3	1.0	24	6	27	16	1000 ppm Na_2SO_4
				1.0	50	12	30	16	
				1.5	50	10	18	12	
D-3	125	35	10.9/2.3	1.5	50	8	6	13	1000 ppm Na_2SO_4
				1.5	85	11	21	13	
D-5	125	35	10.4/4.0	0.5	50	9	61	18	2000 ppm Na_2SO_4
				0.5	100	11	70	22	
				0.5	150	13	82	22	
				0.5	200	16	89	25	
D-6	125	35	10.4/4.0	1.0	100	9	64	23	2000 ppm Na_2SO_4
				1.0	200	16	41	12	
D-8	125	35	10.8/2.3	0.5	25	6.5	66	25	1000 ppm Na_2SO_4
				0.5	50	8.6	47	15	
				0.5	75	10	63	20	
				0.5	100	12	73	20	
D-9	125	35	10.8/2.3	1.0	50	8.4	66	21	1000 ppm Na_2SO_4
				1.0	100	12	38	11	
				1.0	150	15	45	11	
				1.0	190	17	54	11	

TABLE 5

RESULTS OF PILOT-PLANT UNIT TEST RUNS AT AI -
USING ONE 2-1/4 IN. GRAPHITE ROD AS ANODE COLLECTOR
AND SODIUM SULFATE AS SUPPORTING ELECTROLYTE

Run No.	Solution Conditions			Flow Rate (gpm)	Current (amp)	Voltage (volts)	% Cd^{++} Removal	% CN^- Removal	Remarks
	CN^- (ppm)	Cd^{++} (ppm)	pH/Conductivity $10^{-3}\ \Omega^{-1}\ cm^{-1}$						
D-22	125	35	10.8/2.3	0.5	10	5	1	25	1000 ppm Na_2SO_4
				0.5	15	5.8	21	15	
				0.5*	30	8.8	32	11	
				0.5*	45	11.0	39	4	
D-23	125	35	10.8/2.3	1.0	25	6.7	27	18	1000 ppm Na_2SO_4
				1.0	50	9.0	36	7	
				1.0	90	11.6	52	7	
D-24	125	35	10.9/4.0	0.5	10	5.2	73	34	2000 ppm Na_2SO_4
				0.5	15	5.6	68	31	
				0.5	30	7.2	72	23	
				0.5	65	9.4	81	22	
D-25	125	35	10.9/3.9	1.0	25	6.6	49	26	2000 ppm Na_2SO_4
				1.0	50	9.2	61	22	
				1.0	100	12.7	70	22	

* Pressure build-up in tin bed due to plugging

of O_2 was believed actually to be hindering the oxidation of cyanide by blocking the graphite bed surface. Chlorine (or ClO^-) was expected to supplement the electrochemical oxidation of CN^- with chemical oxidation. The results confirmed the expectation that NaCl was a better supporting electrolyte for cyanide oxidation. These are summarized in Table 6 and discussed below.

c. Results with the Final Cell Design

As high as 60% of cyanide removal was obtained using NaCl as the supporting electrolyte while the highest removal obtained with Na_2SO_4 was 34%.

In order to improve the transfer of CN^- to the graphite surfaces in the particle bed, to distribute the electrolytically generated Cl_2 (or ClO^-) more uniformly, and to increase the contact time of this Cl_2 with the water, recirculation of part of the water flowing through the graphite bed (anode) was tested. Approximately 75% of the flow was recycled so that at a net flowrate of 0.5 gpm, the flow through the graphite bed was about 2.0 gpm. With this recirculation through the graphite bed, cyanide removal of 77% was obtained compared with 60% removal without recirculation. The corresponding cadmium removal was 97% compared with the highest previous removal of 81% without recirculation. These were the best results obtained in the testing of the pilot-plant unit at AI using the synthetic wastewater.

d. Discussion of Results

(1) Introduction

The overall objective in operation of the pilot-plant unit at AI was to test cadmium and cyanide removal using the synthetic wastewater and to determine the effect of several operating parameters on these removals. This objective was successfully achieved. Based on the results obtained the effects on the cadmium and cyanide removal of, (a) the type and amount of the supporting electrolyte, (b) flowrate, (c) graphite bed recirculation, and (d) the applied current are summarized in the following sections.

(2) Type and Amount of the Supporting Electrolyte

For cyanide removal, better results were obtained with NaCl rather than with Na_2SO_4 as the supporting electrolyte and at a higher concentration of the supporting electrolyte, i.e., 2000 ppm vs 1000 ppm. It is believed that the cyanide concentration was reduced both by electrochemical oxidation, and by chemical reaction with chlorine or hypochlorite ion generated in the anode bed.

Chorine or hypochlorite generation involves the reaction:

$$2\ Cl^- \longrightarrow Cl_2 + 2e^-$$, possibly followed by the reaction:

$$H_2O + CL_2 \longrightarrow HCl + HClO$$

TABLE 6

RESULTS OF PILOT-PLANT UNIT TEST RUNS AT AI -
USING 2-1/4 IN. GRAPHITE ROD AS ANODE COLLECTOR AND SODIUM CHLORIDE AS SUPPORTING ELECTROLYTE

Run No.	Solution Conditions			Flow Rate (gpm)	Current (amp)	Voltage (volts)	% Cd^{++} Removal	% CN^- Removal	Remarks
	CN^- (ppm)	Cd^{++} (ppm)	pH/Conductivity $10^{-3}\ \Omega^{-1}\ cm^{-1}$						
D-26	125	35	10.8/3.0	1.0	25	7.3	62	23	1000 ppm NaCl
				1.0	50	10.0	56	23	
				1.0	85	13.4	64	28	
				1.0	10	4.0	42	22	
D-27	125	35	10.8/3.0	0.5	10	8.9	52	25	1000 ppm NaCl
				0.5	15	12.2	58	34	
				0.5	25	12.0	70	35	
D-28	125	35	10.8/4.9	1.0	10	5.5	62	13	2000 ppm NaCl
				1.0	25	9.7	58	22	
				1.0	50	12.7	66	37	
D-30	125	35	10.8/4.9	0.5	10	4.7	47	37	2000 ppm NaCl
				0.5	25	7.4	61	43	
				0.5	50	10.5	67	52	
				0.5	100	14.5	76	60	
				0.5*	100	11.8	91	52	
D-31	125	35	10.8/4.9	0.5*	10	3.7	88	35	2000 ppm NaCl
				0.5*	25	6.2	85	53	
				0.5*	50	8.9	93	72	
				0.5*	100	12.4	96	77	
				0.5*	125	14.0	97	77	

* Recirculation; net flow = 0.5 gpm tin bed = 0.5 gpm graphite bed = 1.8-2.0 gpm

Cyanide oxidation then involves the reactions:

$$CN^- + 2OH^- \longrightarrow CNO^- + H_2O + 2e^-,$$

$$CN^- + NaClO \longrightarrow CNO^- + NaCl, \text{ or}$$

$$2OH^- + CN^- + Cl_2 \longrightarrow CNO^- + 2Cl^- + H_2O$$

For cadmium, about the same % removals were obtained in the test runs with 2000 ppm of Na_2SO_4, and with 1000 and 2000 ppm of NaCl. With 1000 ppm of Na_2SO_4, lower cadmium removal was obtained. These data are shown graphically in Figures 9 and 10.

(3) Flowrate

The effects of flowrate on the cadmium and cyanide removals are shown in Figure 11. Almost the same percent of cadmium removal was obtained at a 1.0 gpm flowrate as at an 0.5 gpm flowrate.

For cyanide removal, a higher percent removal but a smaller net amount of removal were obtained at the lower flowrate. For example, at 50 amperes, 52% (or 123 mg/min) and 37% (or 175 mg/min) of cyanide removals were obtained with flowrates of 0.5 gpm and 1.0 gpm, respectively.

(4) Recirculation Through the Graphite Bed

Comparative results, with and without recirculation, are shown in Figure 12. Recirculation through the graphite bed was found to enchance both cyanide and cadmium removals. For example, without recirculation with a flow rate of 0.5 gpm and a cell current of 50 amperes, 67% cadmium removal and 52% cyanide removal were obtained. With recirculation of approximately 3/4 of the anode effluent at the same overall operating conditions, 93% cadmium removal and 72% cyanide removal were obtained. These better results were probably due to the following: (a) higher rate of transport of CN^- to the graphite bed particles, (b) better contact for a longer time of the CN^- with the evolved Cl_2, and (c) additional Cd removal in the graphite bed by (1) release of Cd^{+2} from $Cd(CN)_4^=$ upon oxidation of CN^-, followed by (2) precipitation of $Cd(OH)_2$ and its removal by filtration in the bed.

(5) Applied Currents

Figures 9 to 12 show the effects of the applied current on percent cadmium and cyanide removals at various operating conditions.

With NaCl as the supporting electrolyte, increasing the current beyond about 50 amperes gave only marginally greater cadmium and cyanide removals. With Na_2SO_4 as the supporting electrolyte, the same pattern for cadmium removal was observed, while cyanide removal decreased with increased current beyond 10 amperes. This was explained earlier by the blocking action of evolving oxygen. It should be noted that with higher concentrations of Cd^{+2} and CN^-, the current beyond which increases in removal are marginal would be greater.

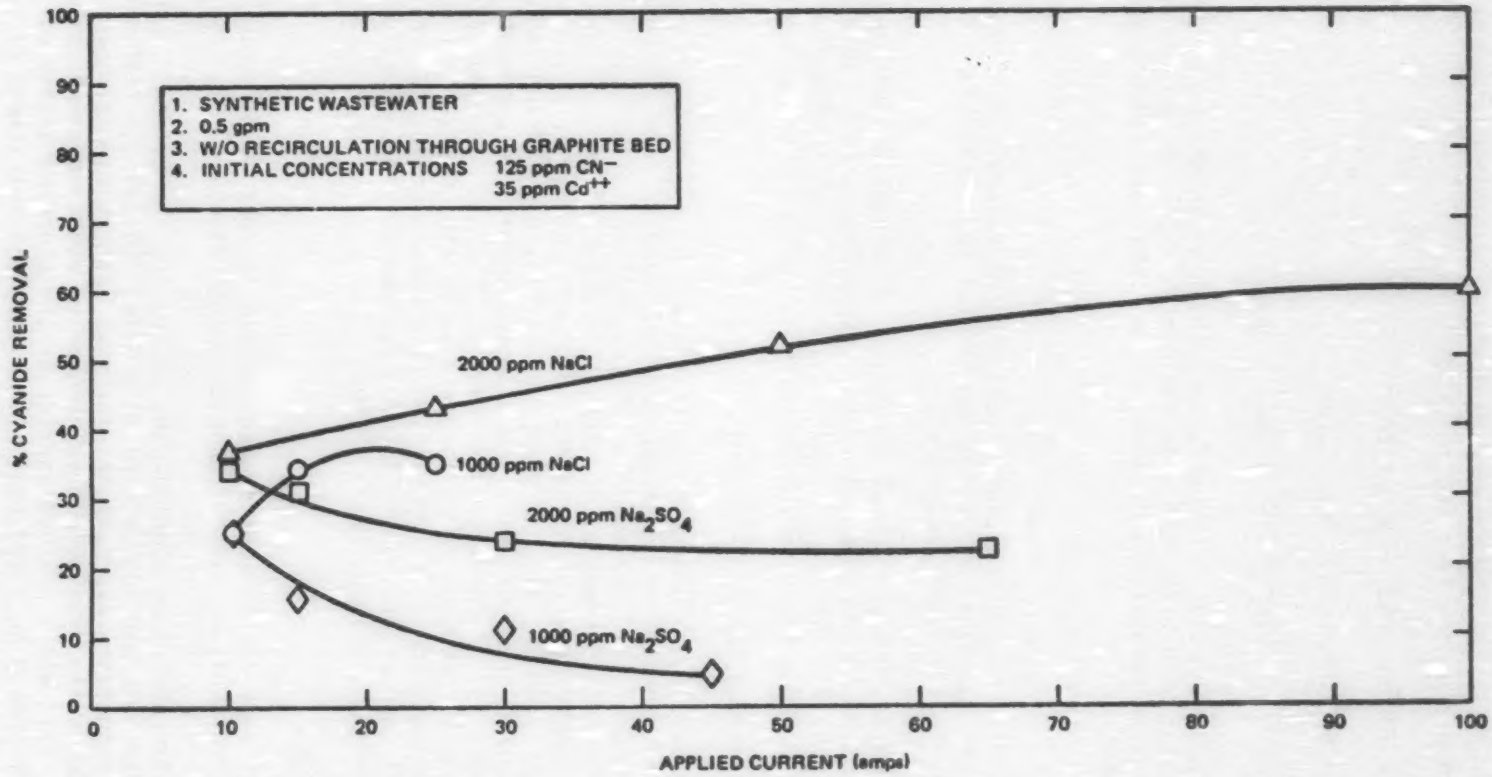

Figure 9. Effects of the Supporting Electrolytes on Cyanide Removal

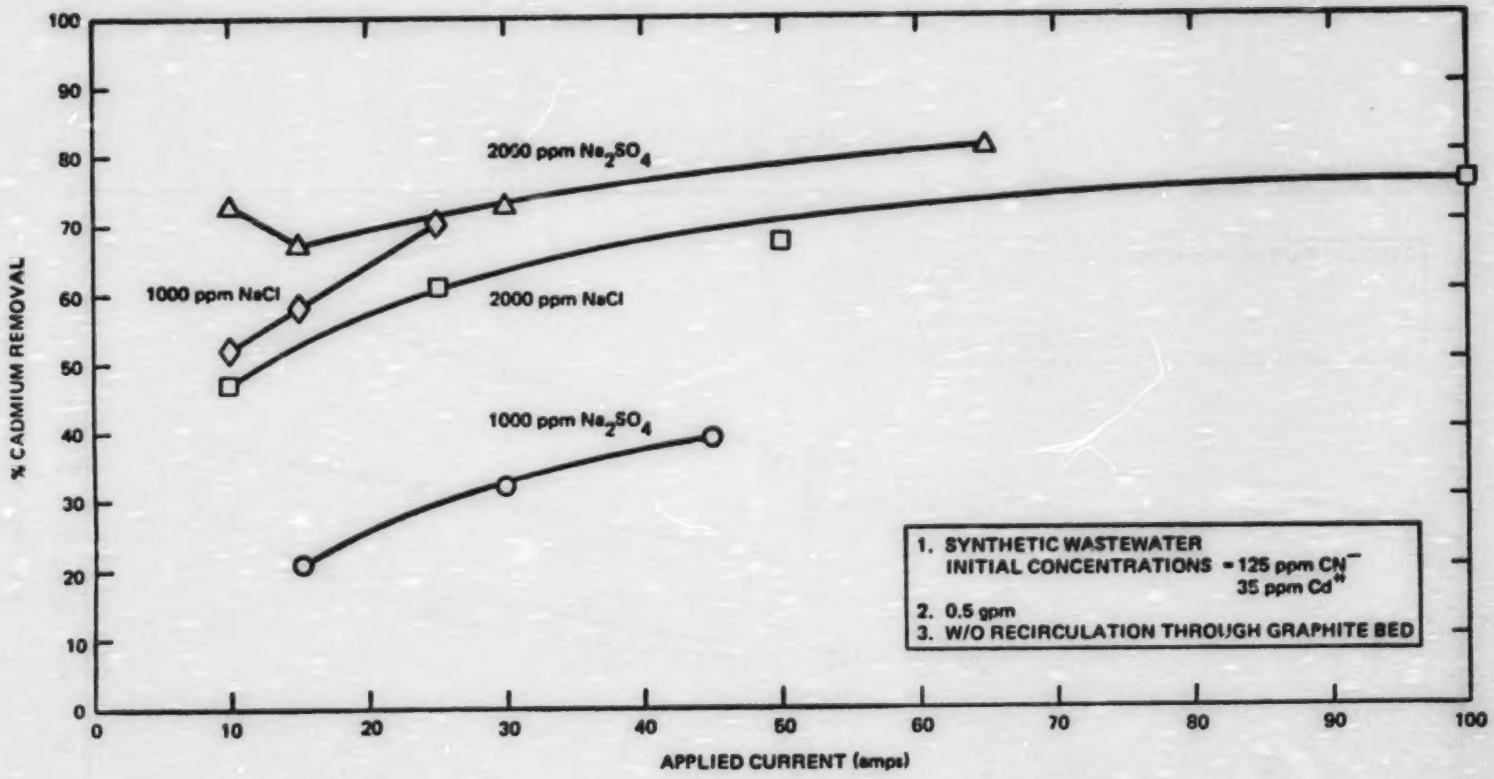

Figure 10. Effects of the Supporting Electrolytes on Cadmium Removal

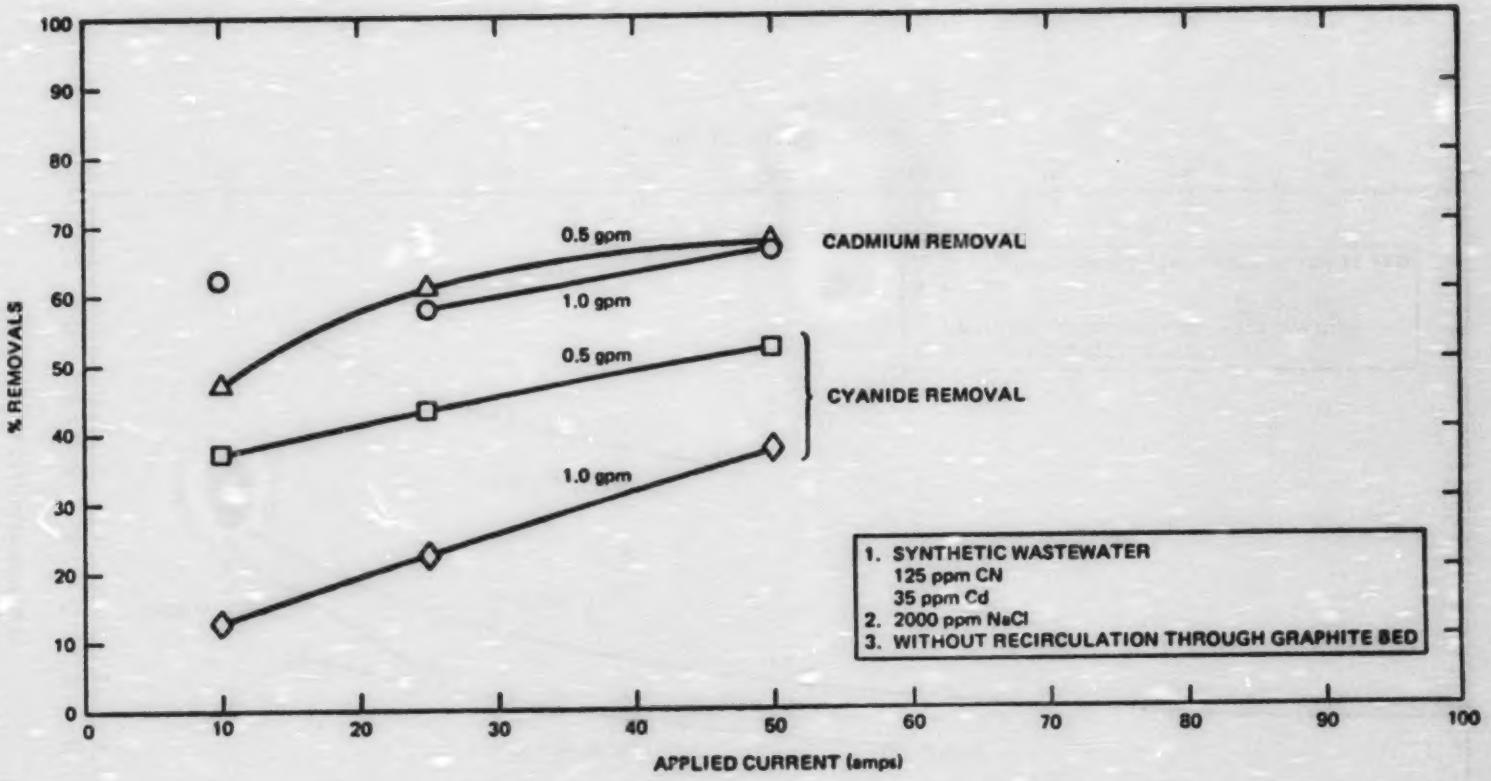

Figure 11. Effects of Flow Rates on Cadmium and Cyanide Removal

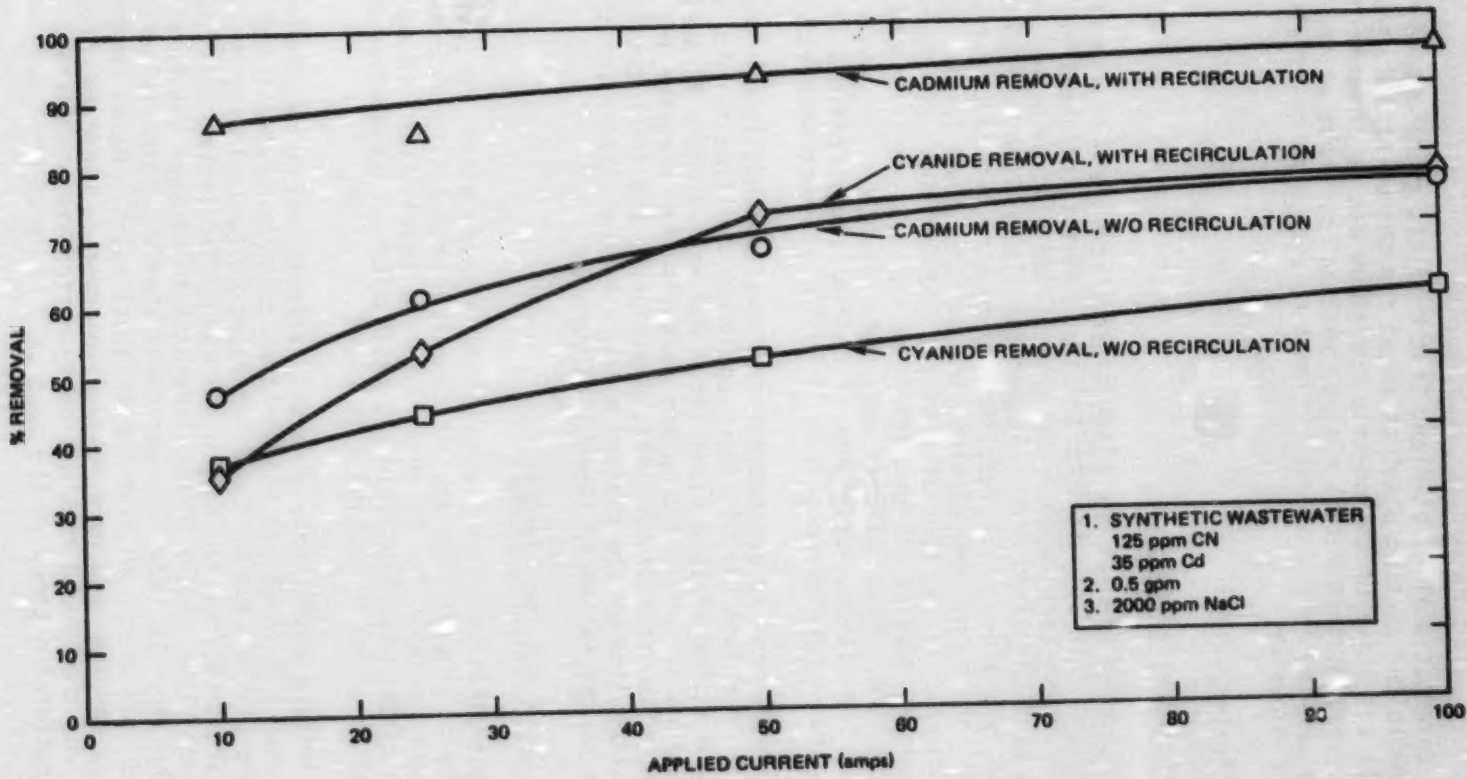

Figure 12. Effects of Recirculation Through the Graphite Bed on Cadmium and Cyanide Removal

B. OPERATION OF THE PILOT-PLANT UNIT AT THE PLATING PLANT

The Atomics International Pilot-Plant Test Unit was shipped on a shock-resistant platform to the plating plant selected for the on-site demonstration. The overall objective of the on-site operation was to demonstrate metal and cyanide removal from actual plating wastewater. Most of the testing was done on a cadmium line drag-out rinsewater, with some tests also made with a zinc line rinsewater.

1. Cadmium Wastewater

a. Operating Procedures Adopted

Operating procedures used at the plating plant were essentially the same as those used for synthetic solutions in tests at Atomics International. Wastewater from the first (drag-out) rinse tank of the plating plant rinse system was pumped to a 55-gallon drum. Supporting electrolyte, either NaCl or Na_2SO_4 solution, was added. The resulting wastewater, which contained 1000 to 2000 ppm of the supporting electrolyte, was then used for the test runs. Since the barrel plating operation of the cadmium line was a batch system, the cadmium and cyanide concentrations in the drag-out rinse tank varied from time to time. While efforts were made to obtain the wastewater with high levels of impurities, variations of cadmium concentrations from 8 to 131 ppm and cyanide concentrations from 23 to 170 ppm were observed.

Minor changes were made to accommodate the on-site conditions. The 200 amperes, 20 volt Harrison Lab DC power supply was modified for 230 volt - 3 phase AC available at the plating plant (from 208 volt-3 phase AC available at Atomics International). A third pump was installed for transferring wastewater from the rinse tank to the pilot-plant unit, and after testing, back to the wastewater line of the plating plant. A flow diagram for the on-site demonstration of the system is shown in Figure 13.

b. Start-up and Check-out Test Results

After the pilot-plant unit was set up in the plating plant, several preliminary test runs using NaCl as the supporting electrolyte were made. The results are shown in Table 7. In general, these results were in agreement with those obtained using the synthetic wastewater. A comparison between these results is given in Section VIII-B-1-f.

In these preliminary tests, some abnormal currents and corresponding voltages were observed. Several bed regeneration techniques were tried in order to restore the performance of the Pilot-Plant Unit, including NH_3 wash with and without air agitation, and dilute HCl wash. Two probes were then inserted in several positions in the Pilot-Plant Unit to measure the potential drop across the separator and beds. It was found that the potential drop across the separator had increased over the original value. Based on this result, the graphite and tin beds were removed in order to clean and inspect the separator. It was then found that the epoxy-coated stainless steel screen used for structural support in the test cell had been corroded. It

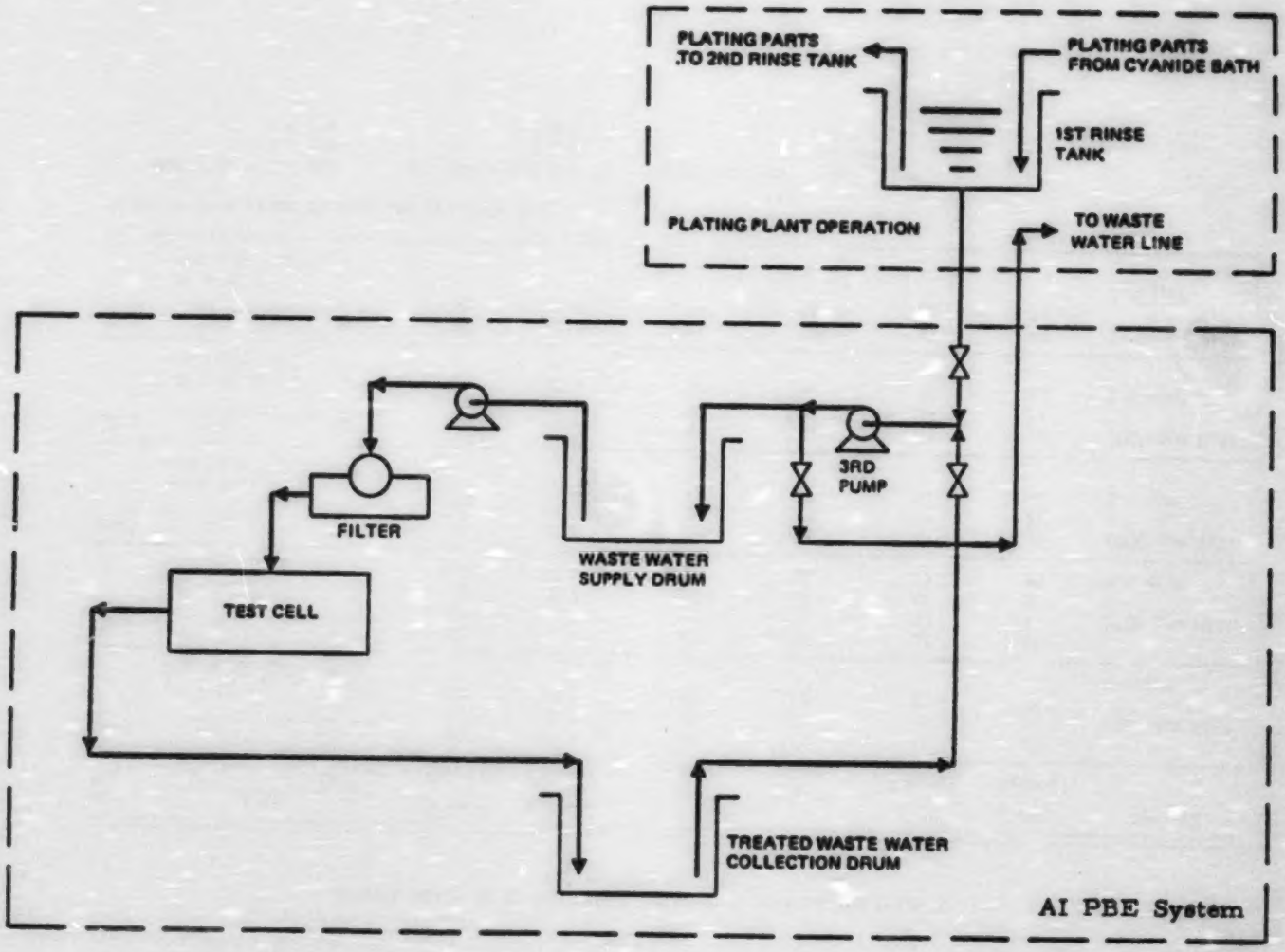

Figure 13. Simplified Flow Diagram for On-Site Demonstration of the Atomics International PBE System

TABLE 7

ON-SITE HEAVY METAL AND CYANIDE REMOVAL DEMONSTRATION RESULTS - PRELIMINARY TEST RUNS

Run No.	Feed CN^- (ppm)	Feed Cd^{++} (ppm)	Current (amps)	Voltage (volts)	Effluent Cd^{++} (ppm)	Effluent CN^- (ppm)	% Cd^{++} Removal	% CN^- Removal	Remarks
00-1	170	131	20	12.2	76	110	42	35	
			35	15.0	56	120	53	30	2000 ppm NaCl
	pH = 10.6		60	16.4	45	110	65	35	
	$\sigma = 6.0 \times 10^{-3} \Omega^{-1}\ cm^{-1}$								0.5 gpm
00-2	120	71	10	4.2	45	105	37	12	
			25	6.8	33	71	53	41	2000 ppm NaCl
	pH = 10.2		50	10.2	24	53	66	56	
	$\sigma = 6.5 \times 10^{-3} \Omega^{-1}\ cm^{-1}$		100	16.0	19	38	73	68	0.5 gpm*
00-3	85	56	35	8.8	29	55	48	35	2000 ppm NaCl
			65	16.1	27	50	52	41	
	pH = 10.1		75	17.0	27	49	52	42	1.0 gpm
	$\sigma = 6.5 \times 10^{-3} \Omega^{-1}\ cm^{-1}$								
00-4	170	95	35	12.0	62	140	35	18	2000 ppm NaCl
			65	16.3	58	135	39	21	
	pH = 10.5		75	17.5	52	130	45	23	1.0 gpm*
	$\sigma = 5.9 \times 10^{-3} \Omega^{-1}\ cm^{-1}$								
00-5	96	41	60	18.5	24	50	41	44	2000 ppm NaCl
			60	16.0	27	66	34	31	
	pH = 10.6								1.5 gpm*
	$\sigma = 5.6 \times 10^{-3} \Omega^{-1}\ cm^{-1}$								

*With recirculation through the graphite bed

Net Flow = 0.5 gpm, 1.0 gpm, 1.5 gpm

Tin Bed = 0.5 gpm, 1.0 gpm, 1.0 gpm

Graphite Bed = 1.8-2.0 gpm, >2.0 gpm, >2.0 gpm

was also found that a piece of small graphite rod, which was threaded to connect the 2nd and 3rd segments of the central graphite rod from the bottom, was broken. This small graphite rod was replaced. The test cell was then reinstalled with a new separator using plastic screen instead of stainless steel screen for structure support.

c. Results of Initial Test Operation

After the test cell was reassembled with the new separator, several sets of test runs were made to investigate the cadmium and cyanide removals from drag-out rinsewater at 0.5 gpm flowrate with 2000 ppm of Na_2SO_4 or NaCl as the supporting electrolyte. Tests were also made using the effluent from test runs as feed to simulate multistage operation, and to investigate the effects of cadmium and cyanide concentrations on the extent of removal obtained. Results from these tests with the new separator are shown in Tables 8 and 9.

In runs with Na_2SO_4 as the supporting electrolyte (Table 8), both with and without recirculation through graphite bed, cyanide removal remained the same or, decreased at currents greater than about 10 to 25 amperes. Similar results had also been obtained with synthetic solutions. With NaCl as the supporting electrolyte, the cyanide removals increased as the current increased over the range of current used. Also, the percent cyanide removal on a second pass was the same as on the first pass at the same flow rate and current.

The cadmium analyses on effluents from the test runs made after the cell was reassembled suggested that cadmium deposited in the tin bed may have become oxidized and was being released to the test solution. Tin bed regeneration was carried out to restore the test cell performance.

d. Bed Regeneration

Tin (cathode) bed regeneration was carried out using an aerated NH_3 solution. Before the ammonia wash, fresh tap water was pumped through the pilot-plant unit for two hours at 1.0 gpm. Then 15 gallons of ammonia solution, which contained 250 grams of NH_4Cl and 500 ml of 28.3% NH_3 solution, was recirculated through the tin bed at 0.5 gpm for about 3 hours. At the end of the ammonia wash, a cadmium sample was taken from the resulting ammonia wash solution. Later analysis showed that the ammonia wash sample contained 9 ppm of cadmium. The ammonia wash solution was then drained from the cell and dumped into the ammonia line of the plating plant.

After the ammonia regeneration, the pilot-plant unit was rinsed with fresh tap water at 1.0 gpm for one hour. Further test runs made after the ammonia regeneration and described in the next section, verified that the tin bed had been cleaned and cadmium removal efficiency restored to the cell.

e. Test Results After Bed Regeneration

The results from the tests run after tin bed regeneration, are shown in Table 10. Two-stage operation was simulated with the first stage using the

TABLE 8

ON-SITE HEAVY METAL AND CYANIDE REMOVAL DEMONSTRATION RESULTS - WITH NEW SEPARATOR AND Na_2SO_4 AS SUPPORTING ELECTROLYTE

Run No.	Feed		Current (amps)	Voltage (volts)	Effluent		% Cd^{++} Removal	% CN^- Removal	Remarks
	CN^- (ppm)	CD^{++} (ppm)			CD^{++} (ppm)	CN^- (ppm)			
OD-20	32	13	10	5.0		18		44	2000 ppm Na_2SO_4
			25	6.3		18		44	
	pH = 9.8		50	7.7		17		47	0.5 gpm
	σ=3.3x10^{-3} Ω^{-1} cm^{-1}		100	12.5		17		47	
OD-21	23	8	10	3.7		11		52	2000 ppm Na_2SO_4
			25	5.1		10		56	
	pH - 9.7		50	6.8		14		39	0.5 gpm*
	σ=3.3x10^{-3} Ω^{-1} cm^{-1}		100	9.7		13		43	
OD-22	17	15	10	4.2		5		71	Treated water
			25	5.9		8		53	from OD-20 is
	pH = 8.0		50	8.5		10		41	used as feed
	σ=3.3x10^{-3} Ω^{-1} cm^{-1}		100	11.8		13		23	0.5 gpm
OD-23	12.5	6	10	3.8		5		60	Treated water
			25	5.5		5		60	from OD-21 is
	pH = 7.9		50	7.0		6		52	used as feed
	σ=3.3x10^{-3} Ω^{-1} cm^{-1}		100	9.8		7		44	0.5 gpm*
OD-29	55	33	10	4.0		34		38	2000 ppm Na_2SO_4
			25	5.2		34		38	
	pH = 11.1		50	7.0		34		38	0.5 gpm*
	σ=4.3x10^{-3} Ω^{-1} cm^{-1}		100	10.2		38		31	
OD-30	36	18	10	3.8		27		25	Treated water
			25	5.0		22		39	from OD-29 is
	pH = 8.5		50	7.4		24		33	used as feed
	σ=4.3x10^{-3} Ω^{-1} cm^{-1}		100	10.6		23		36	0.5 gpm*

* With recirculation through the graphite bed

Net Flow = 0.5 gpm Tin Bed = 0.5 gpm Graphite Bed = 1.8-2.0 gpm

TABLE 9

ON-SITE HEAVY METAL AND CYANIDE REMOVAL DEMONSTRATION RESULTS -
WITH NEW SEPARATOR AND NaCl AS SUPPORTING ELECTROLYTE

Run No.	Feed		Current	Voltage	Effluent		% Cd^{++}	% CN^-	Remarks
	CN^- (ppm)	Cd^{++} (ppm)	(amps)	(volts)	Cd^{++} (ppm)	CN^- (ppm)	Removal	Removal	
OD-25	54	23	10	3.6	15	37	35	31	2000 ppm NaCl
			25	5.1	12	32	48	41	
	pH = 9.5		50	6.9	10	30	56	44	0.5 gpm
	$\sigma = 6.0 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$		100	9.3	17	16	26	70	
OD-26	110	59	10	3.3	27	60	54	45	2000 ppm NaCl
			25	4.8	30	54	49	51	
	pH = 9.8		50	6.4	25	44	58	60	0.5 gpm*
	$\sigma = 6.1 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$		100	6.8	20	33	66	70	
OD-27	27	9	10	3.8	10	22	-	19	Treated water
			25	5.3	16	16	-	41	from OU-25 is
	pH = 8.0		50	7.2	7	14	23	48	used as feed
	$\sigma = 6.0 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$		100	9.5	5	11	44	59	0.5 gpm
OD-28	44	27	10	3.5	8	17	70	61	Treated water
			25	4.8	9	15	67	66	from OD-26 is
	pH = 8.1		50	6.5	7	12	74	73	used as feed
	$\sigma = 6.1 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$		100	9.0	7	7	74	84	0.5 gpm*

* With recirculation through graphite bed

Net Flow = 0.5 gpm Tin Bed = 0.5 gpm Graphite Bed = 1.8-2.0 gpm

TABLE 10

ON-SITE HEAVY METAL AND CYANIDE REMOVAL DEMONSTRATION RESULTS -
CADMIUM LINE WASTEWATER TEST RUNS AFTER BED REGENERATION

Run No.	Feed		Current	Voltage	Effluent		% Cd^{++}	% CN^-	Remarks
	CN^- (ppm)	Cd^{++} (ppm)	(amps)	(volts)	Cd^{++} (ppm)	CN^- (ppm)	Removal	Removal	
OD-31	90	56	25	5.4	47	51	16	43	2000 ppm Na_2SO_4
			25	5.4	46	50	18	44	Added as Supporting
	pH = 10.5		25	5.4	37	51	34	43	Electrolyte.
	$\sigma = 4.0 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$		25	5.4	41	50	27	44	0.5 gpm* Flowrate
OD-32	51	43	25	5.4	29	37	33	27	Treated and
			25	5.4	28	36	35	29	filtered water
	pH = 9.8		25	5.4	23	30	47	41	from OD-31
	$\sigma = 3.8 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$		25	5.4	23	30	47	41	used as feed.
									0.5 gpm* Flowrate
OD-33	44	22	100	9.0	11	9.8	50	78	2000 ppm NaCl
			100	9.0	9	9.4	59	79	Added as supporting
	pH = 9.9		100	9.0	7	9.6	68	78	Electrolyte.
	$\sigma = 5.9 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$		100	9.0	6	9.4	73	79	0.5 gpm* Flowrate
OD-34	9.4	11	100	10.5	2	3.0	82	68	Treated and
			100	10.5	1	2.9	91	69	filtered water
	pH = 8.3								from OD-33
	$\sigma = 5.8 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$								used as feed.
									0.5 gpm* Flowrate

* With recirculation through graphite bed

Net Flow = 0.5 gpm; Tin Bed Flowrate = 0.5 gpm, Graphite Bed Flowrate = 1.8-20 gpm

actual wastewater, and the effluent from the first stage providing the feed for the second stage of operation.

From Table 10, data on two-stage operation may be derived. With Na_2SO_4 as the supporting electrolyte, first stage operation (OD-31) showed 27% cadmium (from 56 to 41 ppm) and 44% cyanide (from 90 to 50 ppm) removal. In the second-stage operation (OD-32) 47% (from 43 to 23 ppm) cadmium removal and 41% (from 51 to 30 ppm) cyanide removal were obtained. The overall results of this two-stage operation were 59% (from 56 to 23 ppm) cadmium removal and 67% (from 90 to 30 ppm) cyanide removal. With NaCl as the supporting electrolyte, first-stage operation (OD-33) showed 73% (from 22 to 6 ppm) cadmium removal and 79% (from 44 to 9.4 ppm) cyanide removal. In the second stage operation (OD-34), 91% (from 11 to 1 ppm) cadmium and 69% (from 9.4 to 2.9 ppm) cyanide removals were obtained. The overall results of the two-stage operation were 94.6% (from 22 to 1 ppm) cadmium removal and 93.6% (from 44 to 2.9 ppm) cyanide removal.

f. Discussion of the Test Results

The effects of the test parameters on the removal results obtained at the plating plant may be summarized as follows:

1) Type of the Supporting Electrolyte

The effects of the types of the supporting electrolyte on cadmium and cyanide removals are shown in Table 11. While the amount of data is limited, it appears that a higher degree of removal of both cadmium and cyanide are obtained with NaCl than with Na_2SO_4. These results were also observed using the synthetic wastewater. They are probably due to the more efficient oxidation of cyanide, plus hydrolysis and filtration of cadmium freed from the complex.

2) Applied Current

The effects of applied current on cadmium and cyanide removals, and comparisons of the test results obtained using both the actual wastewater and the synthetic wastewater with NaCl as the supporting electrolyte are shown in Figures 14 and 15. Both cyanide and cadmium removal increased as the current increased. One hundred amperes appeared to be the limiting current. The cyanide removal results with the actual wastewater were in agreement with those obtained with the synthetic wastewater. Cadmium removal results obtained with the synthetic wastewater were better than those obtained using the actual wastewater.

No data on the effect of applied current on cadmium removal was obtained with Na_2SO_4 as the supporting electrolyte. Cyanide removal appears to decrease with increased current. This was observed with synthetic wastewater and is probably due to the same cause, namely, blocking of the graphite bed by evolving oxygen.

TABLE 11

EFFECTS OF THE SUPPORTING ELECTROLYTE ON CADMIUM AND CYANIDE REMOVALS

Type of the Supporting Electrolye	Run No.	Initial Concentration,* ppm		Final Concentration ppm		% Removal	
		Cd^{+2}	CN^-	Cd^{+2}	CN^-	Cd	CN
2000 ppm	OD-31	56	90	41	50	27	44
$NaSO_4$	OD-32	43	51	23	30	47	41
2000 ppm	OD-26	59	110	30	54	49	51
NaCl	OD-28	27	44	9	15	67	66

*Flow rate = 0.5 gpm with recirculation through the graphite bed (tin bed = 0.5 gpm - graphite bed = 1.8-2.0 gpm). Current = 25 amperes.

3) Initial Wastewater Concentration

The effects of the initial wastewater concentrations on the cyanide removals are shown in Figures 16 and 17. With both Na_2SO_4 and NaCl as supporting electrolytes, the percent cyanide removal decreased as the initial cyanide concentration increased. However, the quantity of cyanide removed increased with increased initial cyanide concentration.

2. Tests With Zinc Wastewater

Demonstration test runs using the wastewater from a zinc plating line were also carried out at the same plating plant. The rinse operation in the zinc line at the plating plant was a continuous system. Two 50 gal. samples of the zinc wastewater were used for these tests. One had 120 ppm of cyanide and 63 ppm of zinc, while the second had 195 ppm of cyanide and 57 ppm of zinc. The test results are shown in Table 12.

As with the cadmium wastewater, a two-stage sequence of testing was carried out. In the first set of tests with Na_2SO_4 as the supporting electrolyte, the cyanide concentration was reduced from 120 to 80 ppm (33% removal) in the first-stage operation (OD-35) and from 85 to 54 ppm (36% removal) in the second-stage operation (OD-36) for an overall removal of 55%. Zinc concentration was reduced from 63 to 19 ppm (69.7% removal) in the first stage (OD-35) and from 22 to 12 ppm (45.5% removal) in the second stage (OD-36) for an overall removal of 81%. With NaCl as the supporting electrolyte, cyanide concentration was reduced from 195 to 115 ppm (41% removal) in the

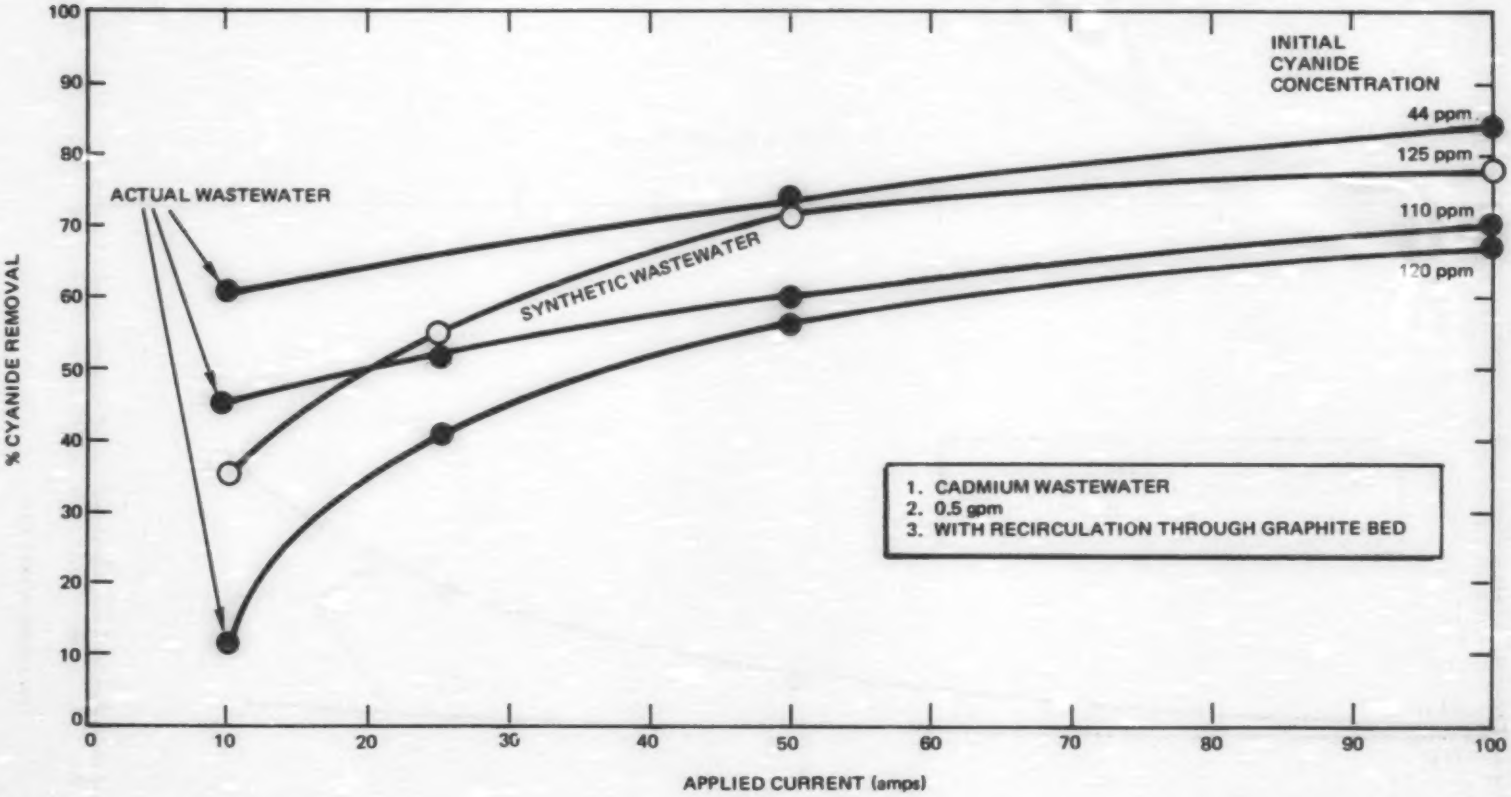

Figure 14. Effects of Applied Current on Cyanide Removal - 2000 ppm NaCl Added

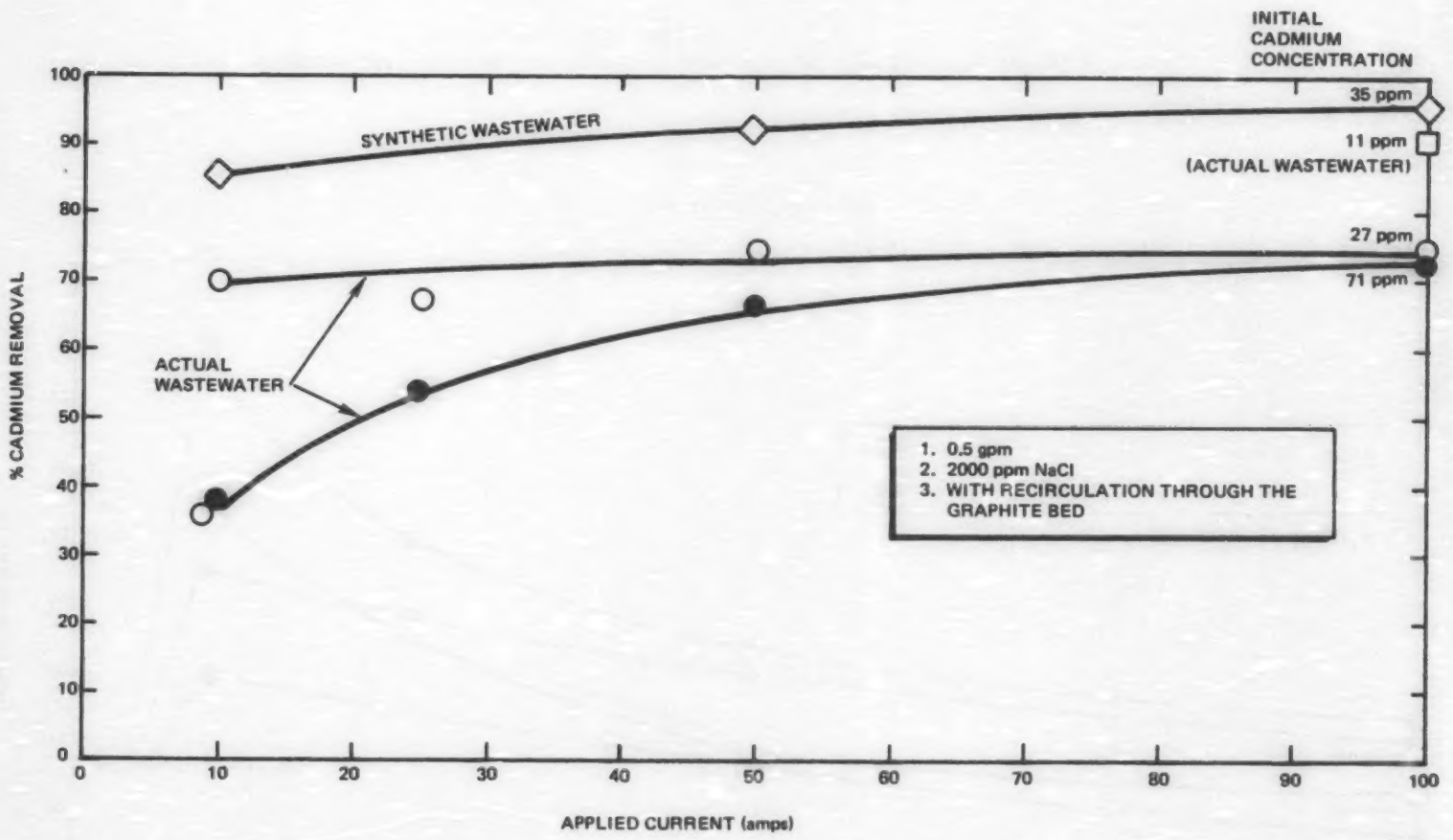

Figure 15. Effects of Applied Current on Percent Cadmium Removal - 2000 ppm NaCl Added

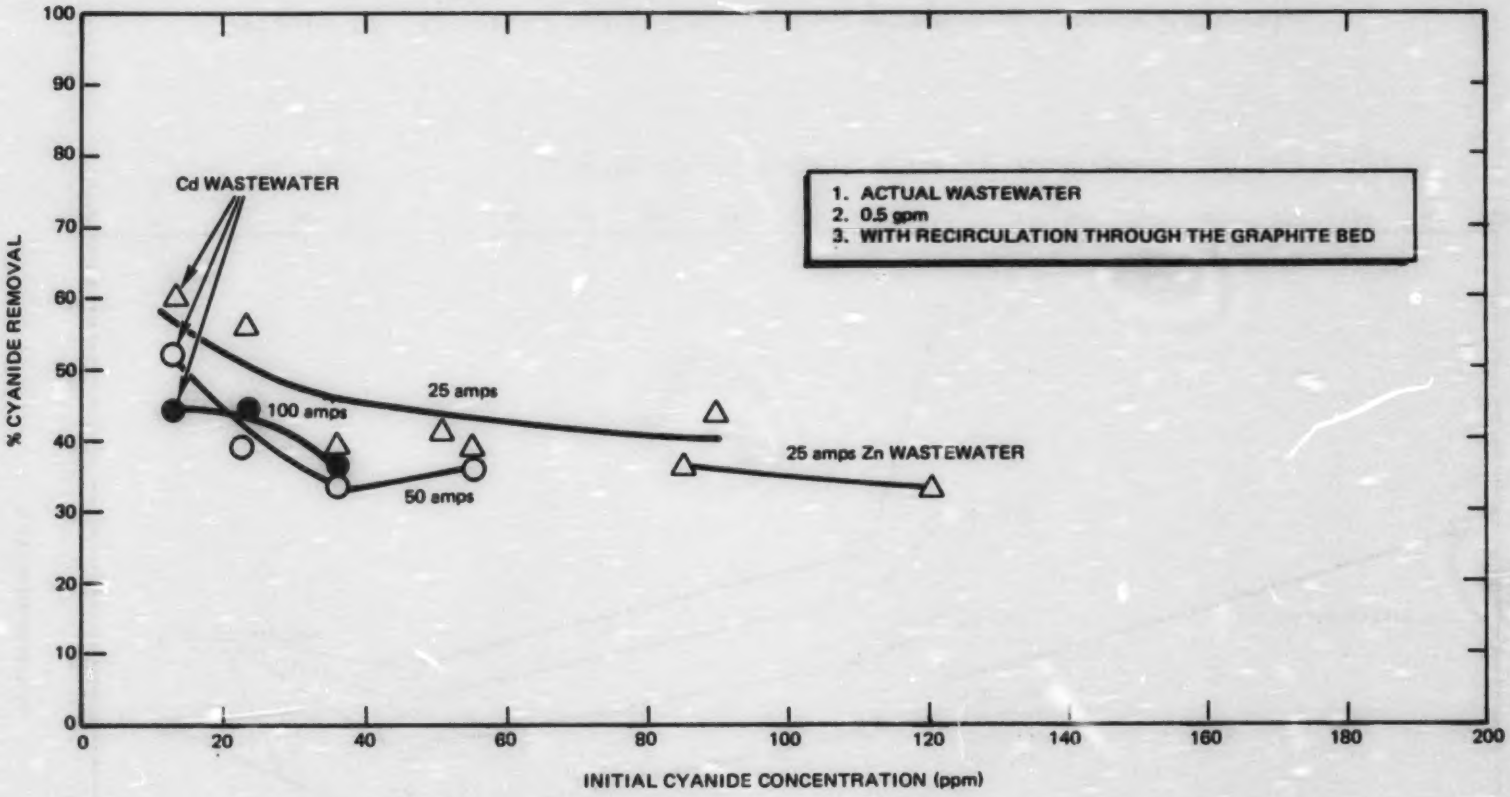

Figure 16. Effects of Initial Cyanide Concentration on Cyanide Removal - 2000 ppm Na_2SO_4 Added

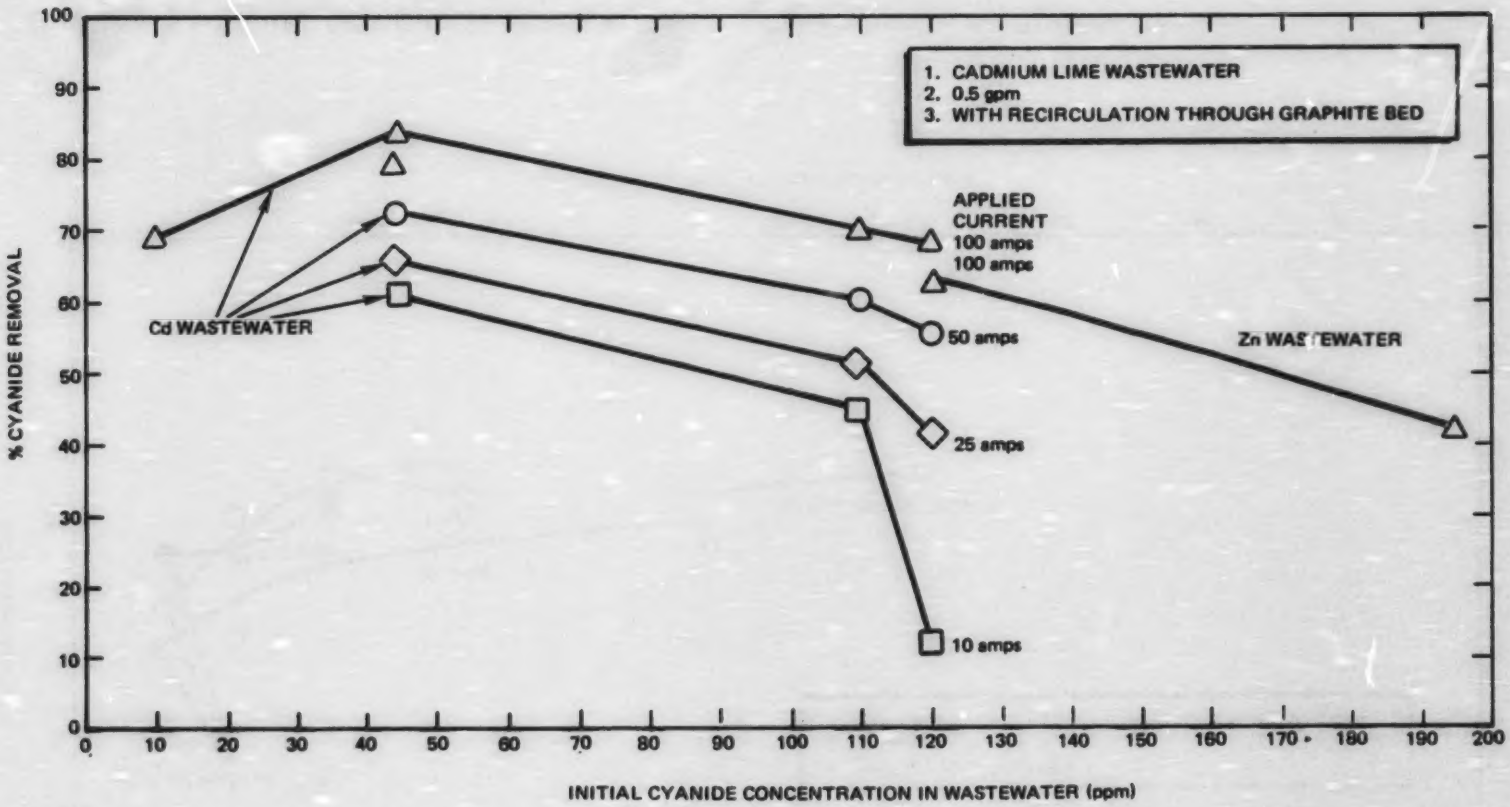

Figure 17. Effects of Initial Cyanide Concentration on Cyanide Removal - 2000 ppm NaCl Added

TABLE 12

ON-SITE HEAVY METAL AND CYANIDE REMOVAL DEMONSTRATION RESULTS -
ZINC LINE WASTEWATER TEST RUNS AFTER BED REGENERATION

Run No.	Feed		Current (amps)	Voltage (volts)	Effluent		% Zn^{++} Removal	% CN^- Removal	Remarks
	CN^- (ppm)	Zn^{++} (ppm)			Zn^{++} (ppm)	CN^- (ppm)			
OD-35	120	63	25	5.0	-	85	-	29	2000 ppm Na_2SO_4
			25	5.0	25	84	60	30	
	pH = 12.2		25	4.7	-	82	-	32	0.5 gpm*
	$\sigma=7.2\times10^{-3}\ \Omega^{-1}\ cm^{-1}$		25	4.7	19	80	70	33	
OD-36	85	22	25	4.9	-	69	-	19	Treated and
			25	4.9	16	70	27	17	filtered waste-
	pH = 11.7		25	5.0	-	55	-	35	water from OD-35
	$\sigma=6.9\times10^{-3}\ \Omega^{-1}\ cm^{-1}$		25	5.0	12	54	45	36	is used as feed 0.5 gpm*
OD-37	195	57	100	9.0	-	120	-	38	2000 gpm NaCl
			100	9.0	30	115	47	41	
	pH = 12.4		100	8.6	-	115	-	41	0.5 gpm*
	$\sigma=9.5\times10^{-3}\ \Omega^{-1}\ cm^{-1}$		100	8.6	29	115	49	41	
OD-38	120	33	100	9.4	-	60	-	50	Treated and
			100	9.4	19	55	42	54	filtered waste-
	pH = 11.3		100	9.2	-	45	-	62	water from OD-37
	$\sigma=7.8\times10^{-3}\ \Omega^{-1}\ cm^{-1}$		100	9.2	14	44	58	63	is used as feed 0.5 gpm*

* Recirculation through graphite bed; net flow = 0.5 gpm, tin bed = 0.5 gpm, graphite bed = 1.8-2.0 gpm

first stage (OD-37) and from 120 to 44 ppm (63% removal) in the second stage for an overall removal of 77%. Zinc concentration was reduced from 57 to 29 ppm (49% removal) in the first stage (OD-37) and from 33 to 14 ppm (57.6% removal) in the second stage for an overall removal of 75%.

The higher overall cyanide removal obtained with NaCl (77%) compared to that with Na_2SO_4 (55%) can be attributed to the added action of free Cl_2 (or OCl^-) produced at the higher current used at the anode. The somewhat lower zinc removal (75% compared with 81%) with NaCl cf to Na_2SO_4 may be due to surface blocking by evolving H_2 gas, or to a lower Zn deposition rate at the higher $[CN^-]$ with a corresponding lower concentration of free Zn^{+2}.

3. Conclusions

The overall objective of the on-site testing at the plating plant was to demonstrate the removal of heavy metals and cyanide from actual wastewater. This objective was successfully achieved. Tin bed regeneration with aerated ammonia solution was also demonstrated.

In a two-stage treatment of the cadmium line wastewater, cyanide concentration in the wastewater was reduced from 110 to 7 ppm and cadmium concentration was reduced from 59 to 7 ppm. These represent 94 and 88% removals of cyanide and cadmium, respectively. In a similar two-stage treatment of zinc line wastewater, cyanide concentration was reduced from 195 to 44 ppm and zinc concentration was reduced from 57 to 14 ppm. These represent 77 and 75% removals of cyanide and zinc, respectively. This indicates that the desired effluent concentration may be achieved by multistage application of the removal process. The treated wastewater can, if desired, be reused as rinsewater.

IX. APPLICATION OF THE PARTICLE BED ELECTRODE SYSTEM TO PLATING PLANT WASTEWATER TREATMENT

A. PLATING WASTEWATER EFFLUENT REQUIREMENTS

Interim regulations concerning the permissible limits on effluent wastewaters are currently being established. It may be anticipated that the permissible federal or federal-approved state levels for heavy metals and for cyanide will be in the range from 1 to 5 ppm for waters entering sewers.

Based on the on-site demonstration test results, a system of this type can easily be operated to meet these wastewater effluent requirements. The ultimate goals set by the EPA for wastewater requirements are likely to be lower. Based on the removals effected during the demonstration tests, and the results of prior tests[2] where zinc and cadmium effluent concentrations below 1 ppm were attained, it is judged that the AI PBE system should be able to meet such limits.

B. METHOD OF APPLICATION OF AI's PBE SYSTEM TO WASTEWATERS

1. Multistage Operation

Multistage operation is a common practice used in various separation processes. This results in effective utilization of equipments so that capital and operating costs can be minimized. The items of equipment used in the multistage operation may be identical in design, or may vary in detail to accommodate changes in the feed.

Calculations for an operating line were based on demonstration test results in Runs No. OD-2, OD-26, OD-28 and OD-34, and are used here to illustrate the multistage operation of the AI PBE system. These calculations show that the cyanide concentration can be reduced from 120 ppm to 3 ppm or less in three stages. In the first stage, cyanide concentration is reduced from 120 to 39 ppm (67.5% removal). In the second stage, cyanide concentration is reduced from 39 to 6 ppm (84.6% removal). In the third stage, cyanide concentration is reduced from 6 ppm to considerably less than 3 ppm. Treated wastewater from this three-stage operation may proceed to further treatment in a one or two-stage unit to meet regulations of less than 0.5 ppm of cyanide in the wastewater effluent. It should be noted that the removal efficiency, i.e., amount of electricity required per unit amount of cyanide removed, is low (about 10% coulombic efficiency) in the treatment of the very dilute cyanide solutions, e.g., 5 ppm or less.

2. Reuse of the Treated Wastewater

Instead of dumping the treated wastewater, which contains only a very small amount of cyanide, this treated wastewater can be reused as rinse water. By this reuse, the net tap water consumption can be dramatically reduced. The cyanide concentration of the treated wastewater can be relaxed to some extent in such recycle operation so that energy consumption in the wastewater treatment can also be reduced.

3. Preliminary Cost Estimation

The technical feasibility of the AI PBE System has been demonstrated. Based on the actual test results at the plating plant, a preliminary estimate of process economics was made using a) 6-stage operation for wastewater treatment, and b) 3-stage operation of wastewater treatment for in-process reuse of the treated wastewater. These are described in the following sections. It should be noted that the economics of a commercial system would probably be different from those derived here.

a. Electricity Cost for Wastewater Treatment for Discharge

It is assumed that the wastewater feed to the AI System contains 110 ppm of cyanide. Calculations were made which show that cyanide concentration can be reduced from 110 to 0.3 ppm with a 6-stage treatment. In the first stage, cyanide is reduced from 110 to 55 ppm. In the second, third, fourth, fifth, sixth stages, cyanide is reduced to 25, 10, 4, 1.6, and 0.3, respectively. The power requirement was estimated at about 11 kwh per 1000 gallons of wastewater treated.

b. Electricity Cost for In-Process Reuse of the Treated Wastewater

Assuming that the wastewater feed to the AI System contains 120 ppm of cyanide, the cyanide concentration may be reduced from 120 to 13 ppm in three stages. This treated wastewater would be reused as rinse water to pick up cyanide from 13 ppm to about 120 ppm in the rinse tank. Per 1000 gallons of wastewater treated, the power requirement is about 7 kwh. Comparing these two modes of applications, it appears that the in-process reuse of the treated wastewater provides an economic incentive in regard to both capital (3 stages instead of 6) and operating costs. An overall preliminary appraisal of the AI System process economics was made based on in-process reuse of the treated wastewater.

c. Economics of Operation of the System with In-Process Reuse of the Treated Wastewater

Two system sizes, namely 0.5 gpm and 5.0 gpm, were evaluated for the cadmium line wastewater treatment. These are listed in Table 13. For the 0.5 gpm system, it is estimated that the cost for treating 1000 gallons of wastewater is $6.28. For the 5.0 gpm system, the cost would be a little over $2.00. These estimations of operating costs were based on the actual demonstration test results. The capital costs were based on (1) the design of the pilot-plant unit; (2) the costs of material for this unit; and (3) a scaling

down and modification of costs estimated previously for a larger (50 gpm) unit of different design. It should be emphasized that these are only estimates. Nevertheless, they do indicate that treatment using the AI system can be carried out at reasonable costs.

TABLE 13

PRELIMINARY COST ESTIMATION FOR THE AI PBE SYSTEM FOR IN-PROCESS WATER RECYCLE APPLICATION

	0.5 gpm	5.0 gpm
Capital Investment	$3,750	$12,500
Gross Cost	$/1000 gallon of wastewater treated	
Electricity at 4¢/kwh	0.28	0.28
Other operating cost	nil	nil
Capital charge at 30% of capital investment	6.25	2.08
	6.53	2.36
Less Credit		
Water at 25¢/1000 gallons	0.25	0.25
Net Cost	6.28	2.11

*Based on (1) 110 ppm of cyanide removal (from 120 to 10 ppm) and 50 ppm of cadmium removal; (2) power requirement for pumping wastewater contributes less than 0.3% of the total electricity cost; and (3) 250 working days per year.

XI. REFERENCES

1. U.S. Patent 3,899,405 (August 12, 1975), "Method of Removing Heavy Metals from Water and Apparatus Therefor."

2. "Laboratory Demonstration of the Atomics International Process for Removal of Heavy Metals from Water," Final Report to the California Water Resources Control Board, October 1972, AI-73-13.